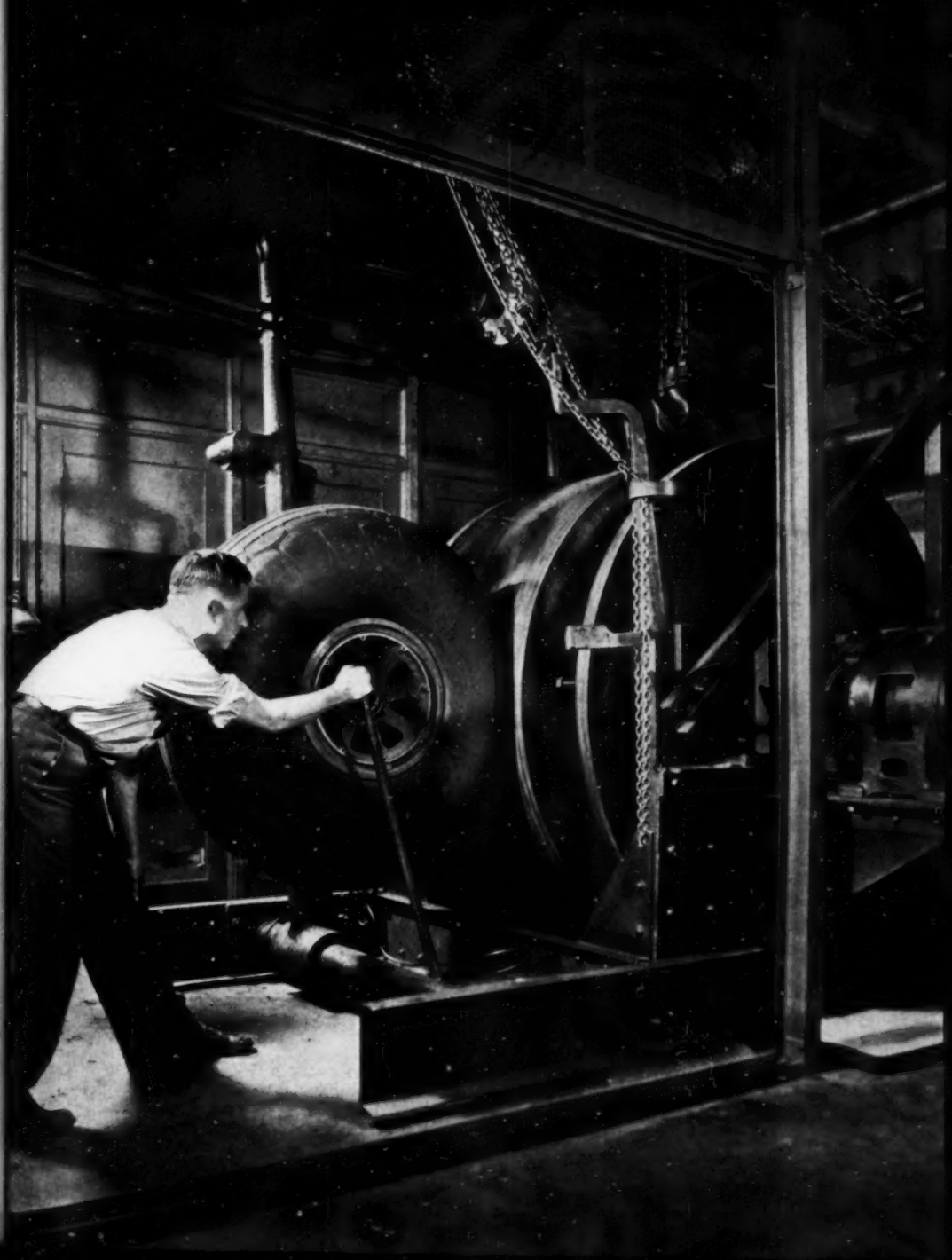
JOURNAL OF APPLIED PHYSICS



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Physics in the Rubber Industry

THE rubber industry provides a particularly fine example of the use of the physicist in industry. It seems that the work of the applied physicist may be classified into two large categories: (1) a study of the fundamental nature of the product, (2) a study of the origin of the raw material and the mechanics of its transformation into the finished product.

In the study of the fundamental nature of the product, the differences between the academic and applied physicist become apparent. Einstein, for instance, speaks for the academic physicist when he states, "Science is the century-old endeavour to bring together by means of systematic thought the perceptible phenomena of this world into as thorough-going an association as possible." The applied physicist on the other hand wants to understand the nature of his product primarily (a) to improve its properties as far as applications are concerned and (b) to extend its uses. The tools and the disciplines which our two physicists use are identical. Thus in the rubber industry we find physicists studying the structure of long chain polymers. They use x-ray and electron diffraction, infra-red absorption, kinetic theory and quantum mechanics. They study such physical properties of rubber as viscosity, hardness, creep, internal friction, thermal and electrical conductivity, dielectric constant, and even optical properties. These studies are correlated with the uses of rubber for those special toroids known as automobile tires, for mattresses, for mounting machines, and for coating wires. As a result of these efforts we find the physicist contributing materially to technological progress and to our personal comfort.

The second phase of the work of the physicist in the rubber industry is just as important as his fundamental studies. He must analyze the sources of the raw materials. Although it is not reported, we can imagine the physicist studying the application of capillarity, diffusion and osmosis to the trees of the genus *Hevea* to increase the amount and quality of the milky exudation. He applies his knowledge of heat transmission to improve the vulcanization processes, of viscosity and hydrodynamics to improve the plastication, and of instruments to control and improve the efficiency of nearly every manufacturing stage. The proof of the value of the physicist in the rubber and other progressive industries is made evident by the ever-increasing demand for his services.

Acknowledgment

THE papers in this special issue on the Physics of Rubber are taken from the Fall meeting of the Ohio Section of the American Physical Society in Akron, Ohio. It is appropriate here to acknowledge the cooperation of Professor H. P. Knauss, Chairman of the Program Committee, Professor R. H. Howe, Secretary of the Section, and Dr. W. F. Busse, our Associate Editor and advisor on problems in the rubber industry. One of the papers presented at the Akron meeting had to be held over and is announced below.

For February

***Physics in 1940*, by T. H. OSGOOD.**

***Plastic Properties of Solids, I*, by F. SEITZ AND T. A. READ.**

***Optical Properties of Rubber*, by L. A. WOOD.**

Contributed Original Research

Physics in the Manufacture and Use of Rubber

BY J. W. SCHADE
The B. F. Goodrich Company, Akron, Ohio

I. Uses of Rubber Depend on Physical Properties

THE rubber industry is today an important part of the world's economic structure. In the United States it ranks as one of our major industries. Its products, valued at about a billion dollars a year, serve every one of us not only directly in the familiar guises of waterproof clothing, garden hose, automobile tires, erasers and rubber bands, but indirectly in many less familiar forms for industrial uses, such as inking rollers and printing plates, rolls for paper-making machines, hoses for handling petroleum products of various kinds and rubber-lined tanks and pipe for the chemical industry (Figs. 1 and 2).

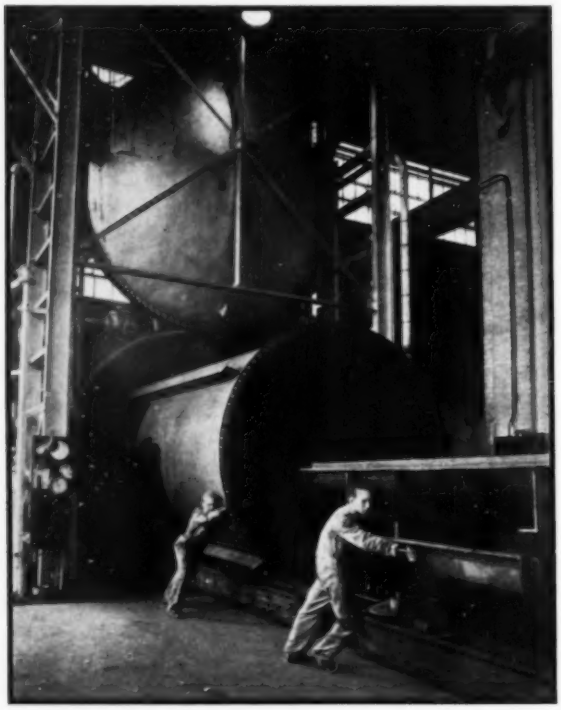

FIG. 1. Removing rubber-lined tanks and fume hoods from a vulcanizer, 15 feet in diameter and 50 feet long.

Rubber is adaptable to so large a number of services because of its unusual stretchability and forceful recovery after deformation, its pliability, its resistance to deterioration under repeated rapid flexure or upon exposure to water, its remarkable resistance to abrasive wear, and its low permeability to certain gases. One or more of these properties makes rubber attractive for each of its myriad applications. In other words, it is the *physical* rather than the chemical features which account for the widespread adoption of rubber goods for personal and industrial uses.

In attempting to duplicate natural rubber by synthesis, chemists have learned that these desirable physical properties do not depend upon chemical composition but rather on the geometric arrangement of the atoms, on the size of the molecules and on the changes in structure imparted by vulcanization processes. In fact, not only have all efforts to duplicate the physical characteristics of rubber by synthesis of identical compositions failed, but improvements in certain properties have been obtained from rubber-like synthetics of decidedly different chemical composition.[1]

II. Contributions to the Rubber Industry by Chemists and Physicists

In spite of this importance of physical properties the earliest scientific work with rubber and most of the striking advances in the industry have been made by chemists, possibly because they were more inclined than the physicists to attack practical problems in a new field. True, the discovery of vulcanization,—the first and most important of the really great inventions relating to rubber,—was made by an investigator who had no formal education in any branch of science; but the processes of reclaiming vulcanized scrap for re-use and of speeding the vulcanization process and improving quality by means of organic accelerators, the development of age resisters to prolong the useful life of rubber, the art of blending with rubber other ingredients to modify its properties,—all these and other important innovations were the contributions of chemists.

Prior to 1906 whatever research of a purely scientific nature was carried out in the rubber industry was presumably performed as a side issue by men engaged with the practical problems of manufacture. It was during that year that George Oenslager entered the employ of the Diamond Rubber Company as the industry's first simon-pure research chemist. Other manufacturers soon followed this lead but it was not until the close of the first World War that research was begun on a substantial scale. Even then emphasis was laid mainly—and by some solely—upon chemical investigations. Our company, however, engaged at that time not only a number of additional research chemists but brought to Akron some physicists, also, to investigate problems outside the realm of chemistry. The results of physical research were so valuable that, as our research staff has grown, physicists, as well as chemists, have been added. The accomplishments attained through physical research, though usually less widely publicized than the results achieved by chemical investigations, have served in numerous ways to improve methods of manufacture, to control operations and quality of goods and to increase our fundamental scientific knowledge of rubber.

It may be said in passing that the life of research physicists in industry does not consist in making prosaic measurements with standard instruments. Great ingenuity and resourcefulness are demanded in designing new experimental methods of studying problems. This usually involves application of the principles of classical physics, with occasional flights into the realms of wave mechanics and electron diffraction phenomena. Rarely, however, are these problems confined to the field of physics alone. Usually they overlap into related fields of chemistry, mathematics and engineering and some knowledge of these allied subjects by the research physicist is essential.

III. Physical Problems in Handling Liquid Latex and Solid Rubber

Almost all natural rubber is obtained today from the milky exudation of trees of the genus Hevea. Acid added to this latex coagulates the suspended rubber particles and crude rubber of commerce is produced by washing, drying, and, quite commonly, smoking the coagulated mass. Most rubber goods are manufactured from this dry material but some articles are made directly from latex compositions containing water suspensions of other ingredients added in order to vulcanize the rubber or otherwise to modify its properties. Each of the suspended particles carries a negative charge and when these are neutralized by positive ions from salt solutions, or from an anode upon passage of a direct current through the suspension, the particles coalesce. Thus gloves are produced by dipping into a bath of latex composition porcelain forms covered with a film of a calcium salt, and rubber coatings are applied to metal articles by placing them as anodes in the bath and passing a current through it. The anode process,[2] first developed independently at the Hungarian Rubber Goods Company of Budapest and the Eastman Kodak Company in America, was perfected in our research laboratories and put into commercial operation in the Goodrich factory. Porous articles also are made directly from latex. Mattresses and seat cushions are familiar examples of this type

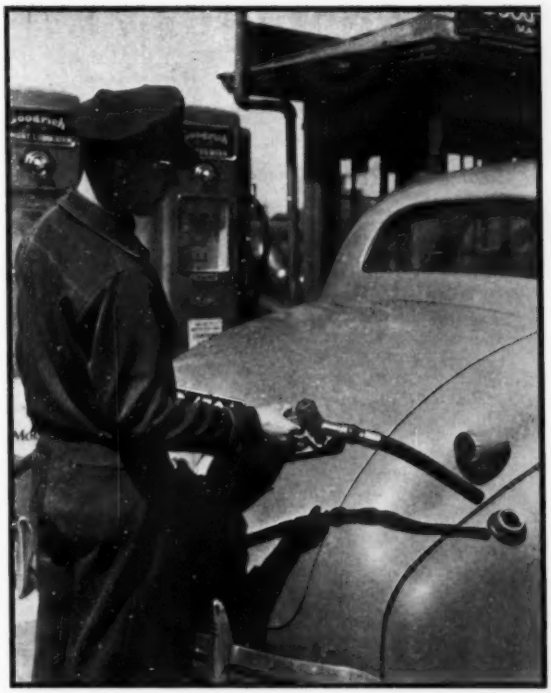

FIG. 2. Gasoline hose nozzle of synthetic rubber. The low electrical resistivity of these compounds prevents sparking from static charges.

of product. The porous structure is formed by frothing or beating and preserved by coagulation before vulcanization and drying. Many physical problems involved in the handling of latex compositions require knowledge of viscosity, hydrostatics, thixotropy, properties of complex dispersions of solids and liquids in liquids as well as the better known principles of heating and cooling, evaporation and the use of electrical circuits.

For manufacturing certain articles of dry rubber, washing and drying is still sometimes necessary, although these operations were greatly curtailed when supplies of rubber from wild growth were supplanted by the cleaner varieties from plantations. Studies of the various drying operations by physicists have yielded valuable information. It was a widely accepted view that drying rubber with heated air caused the surface of the rubber to harden and retard elimination of moisture from underlying portions; and drying methods utilizing partially humidified air were devised to prevent this hardening. Systematic studies, however, indicated that not only was the rate of evaporation induced by dry air at temperatures above those ordinarily used more rapid but that the hotter air caused no damage to the rubber inasmuch as the temperature of the rubber surface did not exceed the temperature of a wet bulb thermometer until shortly before the drying cycle was completed.

IV. Plasticity and Viscosity

Mechanical working of unvulcanized rubber increases its plasticity permanently. Inasmuch as unplasticized rubber is too tough for manufacturing operations it is ordinarily masticated either by milling between rolls or in other types of equipment (Fig. 3). This process has received considerable study by physicists and it was found by Cotton[3] in England and by Dr. Busse[4] in our laboratory that the plastication of rubber involves oxidation. This is induced on mills by activation of the oxygen of the air through static charges produced by working the rubber at comparatively low temperatures. At higher temperatures, in other types of equipment, thermal activation of the rubber molecules promotes oxidation when air or oxygen comes in contact with them. From extensive studies of various plasticating processes knowledge has been acquired of the optimum temperatures required for each and of the effect of catalytic agents to promote the oxidation process. The degree of plastication determines the suitability of the rubber for subsequent operations of sheeting or extrusion. Consequently control measurements of the plasticity of each batch have eliminated large losses previously incurred through efforts to process stock insufficiently plasticized.

Several instruments have been devised for measuring the plasticity of rubber. The Williams plastometer[5] measures decrease in thickness through radial flow of a loaded sample between parallel plates in a definite interval of time. Originally no consideration was given to recovery after deformation but it is now customary to determine this important characteristic also. Another method, first suggested by Marzetti[6] of the Pirelli Rubber Company, Milan, Italy, is based on the assumption that viscosity is the main determining factor of plasticity. Rubber is extruded at constant temperature under definite pressure through a standard orifice and the quantity extruded in a given time is taken as a measure of plasticity. Here again recovery of the rubber was ignored but other investigators later suggested that a measure of the recovery factor could be made by comparison of the diameter of the extruded stock with the diameter of the orifice.[7] Mooney[8] of the United States Rubber Company developed an instrument for shearing a sample of rubber of definite volume at constant

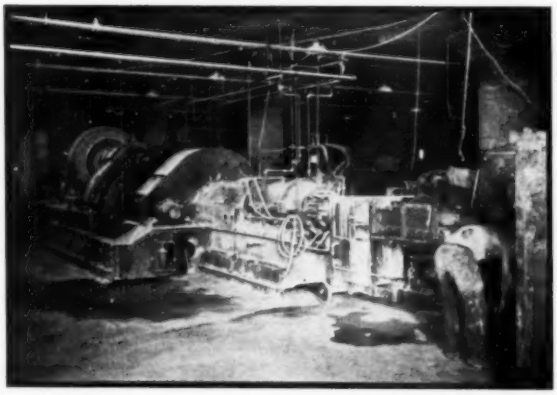

FIG. 3. Plasticator weighing 60 tons mounted on rubber in shear. The entire weight of this machine is supported by rubber in shear through the use of sandwich type flat plate mountings.

temperature between a rotating disk and the walls of a surrounding chamber, using the shearing force as a measure of plasticity. As with the extrusion method, the effect of viscosity largely determines the results.

Karrer, Davies and Dieterich[9] developed the Goodrich plastometer. It is based on the postulate that plasticity involves two factors,—softness and retentivity. A material which deforms readily but recovers almost completely when released from load is not as plastic as one which deforms less readily but retains its deformation. The method involves loading a standard sample with a definite weight for a definite time and, after measurement of the deformation, removing the load and measuring the recovery after a definite interval. The softness, indicated by the deformation, multiplied by the retentivity as determined by the amount of recovery is a measure of plasticity. It has been found that for certain problems one of the two factors may yield valuable information or the ratio of softness to retentivity may be significant.

The viscosity of solutions of rubber in organic solvents decreases as the plasticity of the rubber is increased. Control of the plasticity of rubber intended for the manufacture of cements has, therefore, been useful in maintaining these adhesives at uniform quality. Further control of viscous cements is obtained by application of the falling cylinder test devised by Dr. Busse.[10] Incidentally, rubber is an ideal material for studying the more complicated types of flow, since by milling and adding solvents one can cover almost the whole range of flow properties from the pure elastic deformation of vulcanized rubber to the Newtonian flow of dilute solutions of the highly plasticized unvulcanized material.

V. Heat Studies

Rubber possesses other interesting properties. At low temperatures unvulcanized rubber becomes hard and regains its ordinary condition extremely slowly even at summer temperatures. Heating to higher temperatures or stretching will restore the rubber to its flexible state. In practical operations it is necessary to thaw bales weighing about 220 pounds before they are cut into smaller pieces to be fed to plasticators. Physical studies of heat conductivity of the bales, of the effects of varying the temperature of the heating air, of methods of piling the bales and of other factors have resulted in considerable economy of operation.

FIG. 4. Coating tire cords with rubber. 1600 individual tire cords are brought together in a sheet 60″ wide and coated simultaneously on both sides with thin layers of rubber.

Several examples might be used to illustrate typical applications of physical measurements to factory calendering operations. One of the best is the coating of cords for tire manufacture (Fig. 4). Parallel cords spaced 20 to 30 per inch are run between the rolls of a calender and coated with rubber simultaneously on both sides. It is extremely important for the quality of the tire that the thickness of these coatings be uniform. Control by relative weights of cotton and rubber does not insure equal thickness on the two sides. It is necessary to know that each rubber sheet is of proper gage. Moreover, excess thickness involves heavy losses inasmuch as one thousandth of an inch excess stock for 25,000 tires a day costs about $1000. Consequently the control of gage of the rubber coatings has received considerable attention from our physicists.

One type of gage offered on the market depends on measuring change of magnetic flux with change of thickness of rubber on the calender roll. Another utilizing tuned radio circuits measures the over-all thickness of the coated stock. These have both been thoroughly studied by our

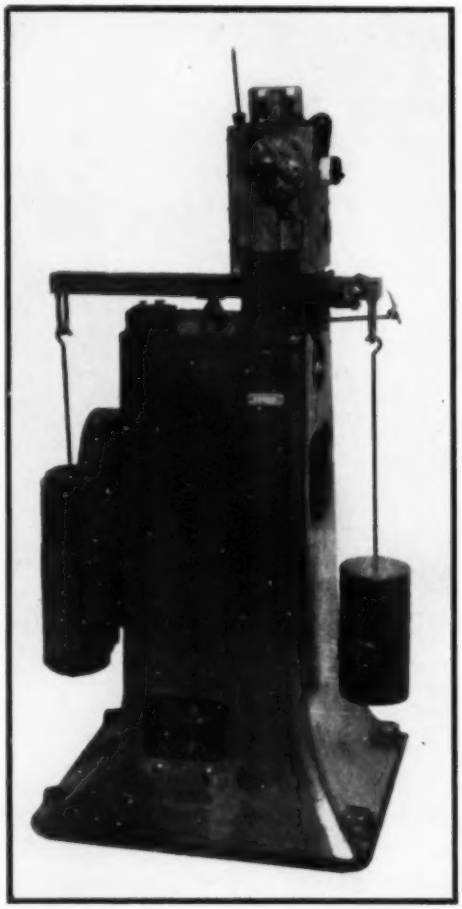

FIG. 5. Goodrich flexometer. Measures the heat generated in rubber compounds by rapid cyclic flexing.

research staff. Both fall short of the requirements they have postulated. Changes in temperature affect their accuracy. The magnetic properties of calender rolls have been found to vary at different points along a roll and around the circumference. Consequently, methods must be devised the accuracy of which will be unaffected either by ordinary changes in temperature or by variations inherent in commercial manufacturing equipment.

The laws of heat conduction and transfer as related to vulcanization processes have also received considerable study. In 1919 when Dr. Blaker began his investigations in this field in our laboratory practically nothing was known of the rate of heating at different points in massive products during vulcanization. By inserting thermocouples at various places in articles and following the temperatures during vulcanization he showed how variable these conditions were. For example, it was discovered that the center of large solid tires vulcanized for three or four hours did not closely approach the impressed temperature until the very end of the vulcanization period. As a result of Dr. Blaker's studies the vulcanization cycles were changed to insure uniform heat treatment of all parts of articles. It was discovered, too, that the transfer of heat from steam coming in contact with goods was often seriously retarded because air inside the vulcanizer was not thoroughly displaced by steam.[11] Piping of heaters was changed to insure thorough elimination of air, presses were modified to remove condensate from the bottoms of steam cavities and so on. These changes brought improvement in the uniformity and quality of many articles. Improvements in vulcanization of hard rubber complicated by exothermal generation of heat and of footwear vulcanized in dry air were also secured. Additional studies embraced other problems involving heat transfer,—the cooling of mill rolls or of extruded tire tread strips. Nowadays, it is possible by computations involving heat conductivity of the rubber compounds (which may be calculated from the conductivities of the various components) and the size and shape of articles, to set conditions of time and temperature of vulcanization without expensive trials with large masses of stock. Occasionally, however, there must still be resort to experimental trials for unusual cases. In an industry utilizing transfer of heat at almost every step of processing, application of physical knowledge has been of great benefit.

Heat is, too, a major factor affecting the service life of rubber goods. The amount of heat developed in rubber by rapidly repeated compressions or elongations is of vital importance, for example, in limiting the life of tires. The measurement of this heat developed through hysteresis has received attention in our laboratories and Dr. Lessig[12] has developed a machine on which tem-

perature rise may be measured (Fig. 5). The test consists in subjecting small blocks of rubber or composite structures of rubber and fabric under an initial definite load to rapidly repeated cycles of compression and measuring the heat generated by means of thermocouples. This has been a most valuable test, enabling tire designers to determine at small cost the relative heating characteristics of rubber compounds without building expensive tires and subjecting them to test on large dynamometers. Even more important is the speeding of development of improved products through saving in time of test and broader experimental attack. It is useful, too, for other problems involving hysteresis phenomena.

VI. Vibration Absorption

Composite structures of steel and rubber are widely used to absorb vibrations caused by moving parts of machinery. Adhesion of the rubber to the steel is secured by electroplating the metal with brass and vulcanizing the rubber in contact with the plated surface. The proper location of these vibro-insulators under machines of non-uniformly distributed weight calls for physical analysis (Fig. 6). Moreover, studies have been carried on for some years measuring the creep of the rubber with time and selecting the best designs and compositions to reduce this to a minimum. As a result of Mr. Hahn's investigations in this field vibro-insulators can now be designed to serve satisfactorily for many years. One of numerous applications of these in our own plant is a support for an 80-ton unit comprising motor, reduction gear and plasticator. A plasticator is shown in Fig. 3. Vibrograph measurements show reduction of 85 percent of the floor vibration in the vicinity of the machine.[13]

VII. Hardness, Tearing and Abrasion Tests

It seems inconsistent to speak of the modulus of elasticity for rubber inasmuch as the change in elongation produced by added increments of load varies continuously almost to the breaking point of test specimens. Dr. Larrick[14] found, however, that values of Young's modulus for rubber at low elongations could be accurately determined by a method other than elongating a strip. He discovered that the penetration of vulcanized rubber by spherical indentors follows the classical laws

FIG. 6. Rubber springs for automobiles. Torsilastic bushings in this car take all the road shocks, giving independent wheel suspensions without the use of any metal springs.

of elasticity based on infinitesimal deformations (Hertz theory) for penetrations as large as 10 percent of the diameter of the indentor and even up to 30 percent does not deviate greatly from theory. Values of Young's modulus calculated from his experimental data range from about 200 psi for soft rubber compounds to over 1000 psi for heavily pigmented stocks. Since resistance to penetration is ordinarily considered to be a measure of hardness, the elastic modulus thus determined may be used as a measure of hardness. Hardness of rubber compounds is of great importance inasmuch as many purchasers' specifications call for a definite value of this property. Dr. Larrick's investigations beautifully illustrate the development of a practical method of test suggested by knowledge of classical theory.

The resistance of rubber compounds to tear is often vitally important, also. Although Dr. Ayres,[15] formerly of our laboratory, long ago proposed a method for measuring tear resistance and others have proposed methods of test, one which meets with general acceptance has yet to be developed. Dr. Busse[16] carried out an interesting series of tests which disclosed some unexpected and interesting phenomena. He compared the behavior of various rubber compositions when subjected to tearing forces with what should have occurred according to theoretical considerations of an ideal, highly elastic, isotropic medium and obtained valuable evidence

concerning the structure of rubber itself and the changes in properties imparted by compounding ingredients. The behavior of rubber under rapid cycles of stress which he described has proved of considerable interest and value to engineers concerned with applications of rubber.

A method for measuring abrasive wear of rubber which will be generally acceptable is, as in the case of tear testing, yet to be developed. Several test machines are in use but the results obtained from the various types do not indicate the same relative wear of various compounds. Most of the tests involve relative movement of loaded test specimens and an abrasive surface. Some indicate rate of wear by loss of weight or volume of the samples, one measures the work expended in wearing away unit volume. In many cases the tests are run under conditions of load or against a surface which do not simulate the conditions the rubber will encounter in service. Consequently the results are of little significance. We have been studying this problem for several years and are now ascertaining the conditions of test under which results are truly indicative of service performance.

Examples of how the physicist has contributed to our knowledge of the properties and processing of rubber and its compounds might be multiplied, but a sufficient number of cases have been cited to indicate clearly the value of physical research in these fields. The physicist's assistance has been sought, too, in other fields. Textile fabrics are of great importance to the rubber industry. Pneumatic tires, conveyor and transmission belting, hose and footwear, all utilize large quantities of cotton, wool or rayon fabrics and the physicist has given his attention to these.

VIII. Textile Fiber and Fabric Studies

Systematic studies of the construction of cords for tires has radically changed concepts of what properties are essential. It once was thought that cords must possess high elongation to avoid rupture under road shocks. It is now realized, however, that most of this elongation is soon lost because the cords undergo permanent stretch, partly during manufacture and partly in service. Today, cords possessing relatively low elongation but greater elastic recovery have been adopted. Mathematical treatment of cord structure consisting of a threefold system of helixes is so difficult that less elegant but more effective methods of experimental physics have necessarily been employed to study the relative values of different cord constructions. Comparisons of the quality of individual cotton fibers as related to age of plants, condition of soil and weather are of great importance. Studies carried on in government laboratories have as yet not covered the problem in sufficient detail.

Other fibers have also received attention. Rayon of special grade, because of its resistance to deterioration at temperatures developed in tires in high speed service, has found a place in the industry. Metal wire, linen, ramie, silk and even glass cords have been made and tested in tires and fan belts with indication of possible improvement of quality in certain cases.

IX. Physics in Designing and Sale of Goods

Physics also aids in the design of articles. Mathematical analysis of stresses developed in an idealized torus, while not directly applicable to the thick-walled composite structure of cotton and rubber in tires, has been of great assistance in directing experimental constructions. One very practical result is a more accurate method of calculating strength of bead wire needed safely to withstand the tension imposed by air pressure in the tire and by road service. Laboratory studies should be further extended to furnish data to the tire designer connecting the properties of cords with bursting strength, bruise resistance and flexing life of tires, belts or other articles. Studies of construction of V-belts used for driving fans and water pumps in automobiles brought improvements which have extended their life under severe test conditions from less than 15 minutes to over six hundred hours and on larger belts of similar type improved the uniformity of strength and stretch and lengthened their service life.

Difficulties arising during the service of goods are often hard to fathom and the laboratories are frequently called upon to solve many mysteries. It was noticed, for example, that the de-icer for the removal of ice which forms on the wings of airplanes during flight (Fig. 7) often developed numerous punctures after only a few months of service. The cause of this was finally traced to discharge of static electricity developed by the

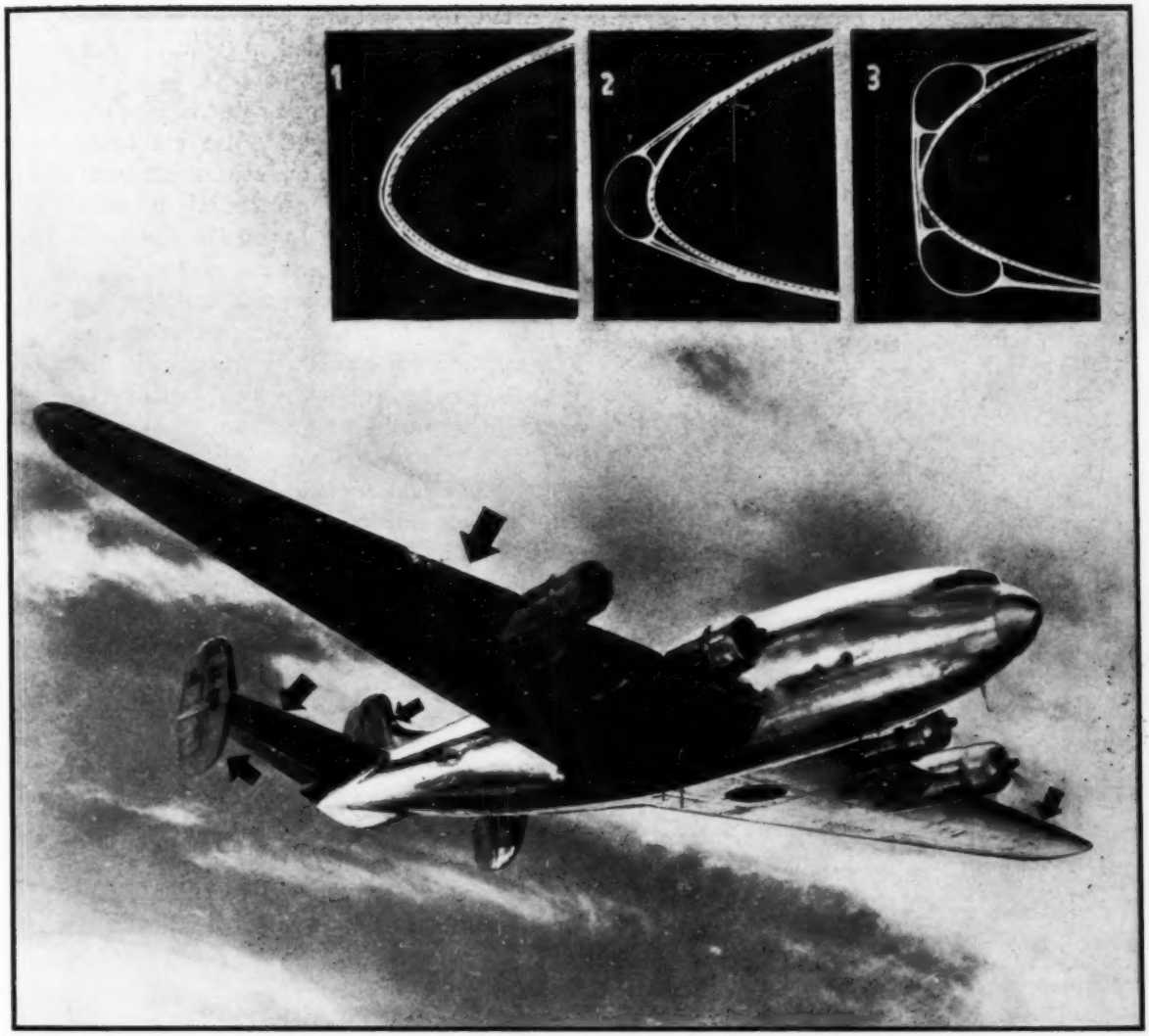

FIG. 7. De-icers. These cover the leading edge of wing and tail surfaces. When ice begins to deposit the alternate inflation of the middle and outer tubes cracks the ice and breaks it away from the surface so that the air stream can remove it.

planes in flight. This static discharge also adversely affected radio reception in the planes. Build-up of these charges was eliminated by coating the rubber with a thin, flexible layer of conducting composition. Again, expander tube brakes used in airplanes were found to squeal, causing discomfort to passengers, especially at night. The resonance of the system was studied and the noise eliminated by changes in design of the rubber portion of the structure (Fig. 8).

The research physicist is called upon not only by the production divisions but by the sales departments. "What," they ask, "makes sponge rubber cushions (Fig. 9) comfortable or uncomfortable? How does the design of the cover of a golf ball affect its flight? Will more water flow through a rubber-lined pipe than through an iron pipe of the same size under the same conditions of pressure?" To find the answers to questions such as these requires not only theoretical consideration of all the factors involved but usually calls for considerable laboratory testing to supply needed data. Orders of considerable value, however, may be secured occasionally only through such information to convince the prospective customer of the merits of the goods.

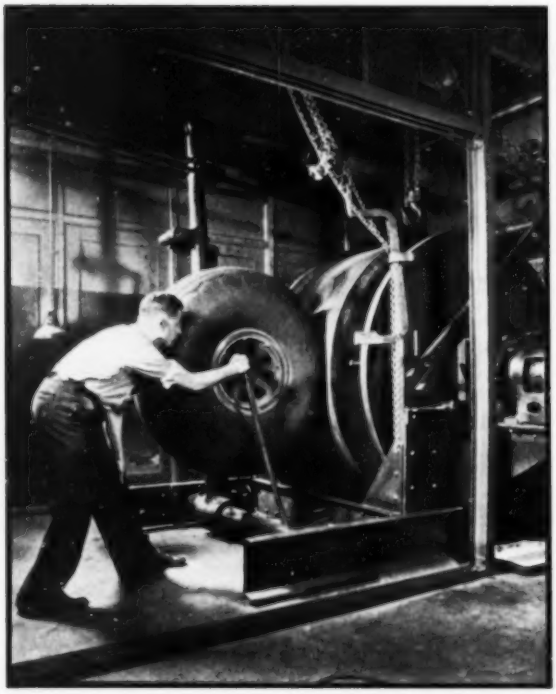

FIG. 8. Lining up airplane tire and brake assembly for life test. Solid metal disks are bolted together to form a mass possessing high inertia. This mass is brought up to speed and then stopped by suddenly forcing the tire against the edge of the disk and applying the brake at the wheel hub. All braking stresses are transmitted through the tire to simulate conditions of an airplane landing.

X. *Fundamental Studies*

All illustrations of physical problems thus far mentioned have been of a practical nature. Physical research, however, concerns itself also with fundamental studies. What is the structure of rubber and rubber-like synthetics? Certain information has been gained by x-ray examination. Unstretched rubber is amorphous unless frozen; but when stretched sufficiently contains a fibrous crystalline phase (to be discussed by Dr. Field of the Goodyear Company). When frozen in a highly stretched condition rubber exhibits a fibrous structure if shattered by hammering.[17] Recently it has been shown that the elastic recovery of stretched rubber is the result of entropy effects within single molecules. (This will be discussed by Dr. Mark.)

Much further information is needed, however, concerning the arrangement of atoms in the molecules of natural and synthetic rubbers and concerning the modification of structure imparted by reactions between rubber and the various finely divided pigments used in its compounds.

Rubber and synthetic rubbers are polymers of high molecular weight. Some are multiples of simple chemical units, others contain two or more polymerizable compounds mixed and copolymerized.[1] Their molecular size is so great that chemical methods are not sufficiently accurate to detect the position and arrangement of the component atoms. Measurement of infra-red absorption (which Dr. Sears will discuss later) gives some indications of their structure but these are by no means adequate to furnish a complete picture of how the molecules are formed. In this important field the industry looks to the physicist for further enlightenment; for it is probable that only some form of physical measurement will yield reliable indications of molecular structure.

FIG. 9. Sponge porosity tester. This instrument measures the porosity of sponge rubber, an important factor in determining comfort.

Recently, examination of carbon black at the University of Toronto by means of the electron microscope has shown the average size of the ultimate crystal units of this valuable reinforcing pigment to be slightly less than 30 mμ. This relatively new tool will undoubtedly broaden our knowledge of materials used in the rubber industry and of the structure of rubber compounds.

Our electrical laboratory has been called upon to investigate the electrical characteristics of rubber and synthetics of various kinds. Koroseal, particularly, because of its adoption in the manu-

facture of insulated wire and cable has received considerable attention. Koroseal is a plasticized polymer of vinyl chloride (Fig. 10). Besides determining the ordinary electrical properties of Koroseal compositions the physicists have been investigating the behavior of polar groups under electrical forces. It has been found that in linear polymers the rotation of individual dipoles is hindered by valence forces along the chain. The experimental data indicate that these dipoles do not respond individually but that fairly long polymer groups behave as units in affecting electrical behavior.

In general it has been demonstrated that physical research has proved of great value in the rubber industry in increasing our knowledge of materials and processes of manufacture and in the design of rubber compositions and articles. Investigations directed toward overcoming operating difficulties and improving quality are supplemented by excursions into fields involving modern physical theory. From the rubber manufacturer's viewpoint physical research is economically justified. To the physicist, industrial physical research is stimulating, calling for the best of his knowledge, ingenuity and originality.

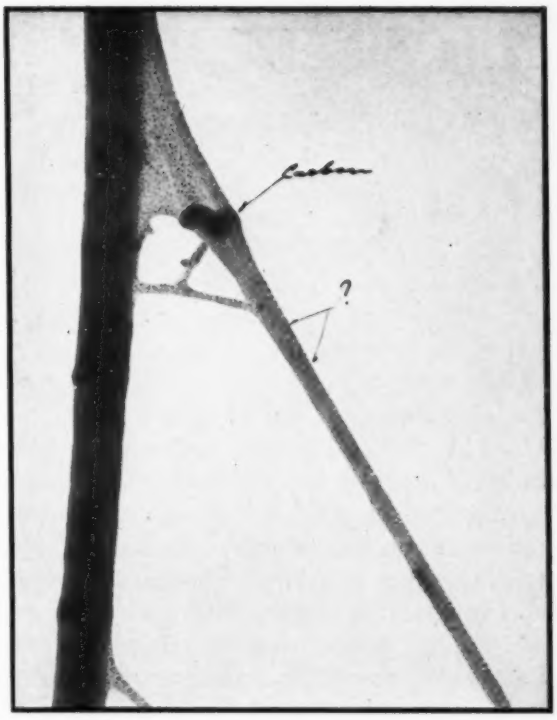

FIG. 10. Electron microscope picture of a film of plasticized polyvinylchloride showing particles of carbon and others which may be vinylchloride micelles. Magnification 44,000. Taken by RCA, 1940.

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Thermal Problems in Rubber Manufacture

BY STUART H. HAHN

Physical Research Laboratory, The B. F. Goodrich Company, Akron, Ohio

I. Introduction

VULCANIZATION, the basic process of the whole rubber industry, is so dependent on temperature that it was named after Vulcan, the God of Fire. Because of the low conductivity of rubber compounds, it is often difficult to heat uniformly the large complex rubber parts required by modern civilization. However, careful studies of the thermal problems involved and the development of "flat-curing" compounds have made possible satisfactory vulcanization of articles ranging in size from one-gram toy tires to enormous "earth-mover" tires weighing more than a ton, or from hundredth-inch diameter thread to massive railroad car springs over a foot in diameter, or even the vulcanization of rubber linings on the large areas inside 10,000 gallon tank cars.

Other heat problems occur in the processing of rubber preparatory to vulcanization. Large quantities of heat are generated by the mechanical working of the plastic masses during mastication, mixing, extrusion or calendering. In most cases this heat must be removed to prevent excessive temperature rise.

Finally, heat problems may be encountered after the fully vulcanized products enter the customer's service. Heat is developed when rubber is subjected to rapid flexure because of its imperfect elasticity, and the low conductivity prevents ready escape of the heat. Such problems are solved by reduction of hysteresis in rubber compounds, and by proper choice and assembly of structural elements for reduction of internal friction and improvement of cooling.

II. Thermal Conductivity and Diffusivity of Rubber

The thermal conductivity of crude rubber has an average value of 0.000375 cal./(sec.)(cm²)(°C/cm). While most of the materials which must be added to crude rubber to give it satisfactory physical properties have somewhat higher conductivities than rubber itself, practical rubber compounds will rarely have as much as two times the conductivity of rubber. The conductivity of rubber is very low, about that of white pine wood, a material once used as an insulator on steam-engine cylinders. It is only about three times as great as that of common porous insulators such as cork-board or rock wool, and it is less than 1/200 as much as that of common metals.

Rubber has not only a low conductivity but also a relatively high specific heat, about 0.48. This makes its volumetric heat capacity about the same as that of metals. Consequently its thermal diffusivity, or ratio of thermal conductivity to volumetric heat capacity, is very low. Thermal diffusivity is a measure of the rate of temperature propagation through a material. The diffusivity of rubber compounds usually lies between 0.0008 and 0.0014 c.g.s. unit as compared with about 0.0015 for soft woods and 0.13 for steel.

The analytical solutions of problems involving heat transfer through solids are based on solutions of the Fourier equation:

$$\frac{dQ}{d\theta}=\rho C\frac{dt}{d\theta}=\frac{\partial}{\partial x}\left(k\frac{\partial t}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial t}{\partial y}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial t}{\partial z}\right),$$

in which Q is the heat density at the point x, y, z in Cartesian coordinates. Graphical solutions of this equation for standard shapes such as spheres, cylinders, plates, etc., can be obtained by the use of the Gurney-Lurie[1] charts which involve four dimensionless ratios:

A temperature difference or an unaccomplished temperature change ratio:

$$Y=\frac{T-t}{T-t_1}.$$

[1] Ind. Eng. Chem. **15**, 1173 (1923); W. H. McAdams, *Heat Transmission* (McGraw-Hill, 1933).

A "relative time" ratio:

$$X=\frac{k\theta}{\rho CR^2}.$$

A relative resistance ratio:

$$m=\frac{1}{h}\Big/\frac{R}{k}=\frac{k}{hR}.$$

A position ratio:

$$n=r/R,$$

where θ = time from start of cooling or heating, C = specific heat of solid, ρ = density of solid, T = constant uniform temperature of surroundings, t = temperature at position n within solid at time θ, h = surface heat transfer coefficient, k = thermal conductivity, r = distance from midplane, R = distance from midplane to surface.

The relative importance of the surface heat transfer coefficient and the thermal diffusivity is illustrated in Table I which shows the times required to heat large slabs 4 cm thick of several materials under two sets of conditions. In the first case the heating medium is gas-free steam where the surface coefficient is very high, estimated about 0.41 c.g.s. unit. In the second the medium is air at low velocity (approx. 2 m/sec.) with the surface coefficients determined experimentally to be 0.00025 for the metals and 0.00016 for the two grades of rubber. The table shows the times required to change the temperature at the center of the slab 50.0 percent and 99.5 percent of the total impressed temperature difference, when the heat is applied uniformly to both surfaces. The effect of changes in the surface heat transfer coefficient on both good and poor conductors is shown by comparing the ratios of the times for 50 percent temperature change of the metals heated in air and in steam (e.g., about 3300 for copper), with the same ratios for the poor conductors (e.g., about 3 for crude rubber). There is a significant difference in this ratio even for the two metals. The important factor determining the ratio of heating times for slabs of a given thickness is seen to be the ratio of the thermal conductivity of the slab to the surface heat transfer coefficient, which is the parameter "m" above. It should be noticed that the ratio of the 99.5 percent to the 50 percent time is almost constant for all materials in a given heat transfer medium, but that it is somewhat greater for slow than for rapid heating.

TABLE I. *Heating times for 4-cm slabs of various materials.*

	Time in Minutes			
	Heating in Gas-Free Steam		Heating in Air	
Temperature change accomplished at center	50%	99.5%	50%	99.5%
Material				
Commercial copper	0.023	0.134	75.5	577
Mild steel	0.196	1.16	77.2	589
Loaded rubber compd.	15.7	93.3	89.5	642
Crude rubber	31.4	186.	93.1	650

While the Gurney-Lurie curves have been useful in analyzing some heating and cooling problems, the majority of problems in the rubber industry do not meet the conditions assumed in developing these curves; namely, uniform composition, uniform surface temperature, known and constant heat transfer coefficient, and simple geometric shape. For these and other reasons, it is usually necessary to solve most thermal problems by the actual measurement of the temperature changes in various parts of the sample being studied.

III. Processing Problems

Study of the cooling of rubber during mixing operations is of considerable importance, because a large amount of work must be done on the rubber to disperse fine powders uniformly throughout the mass, and the temperature must be kept low enough to prevent "scorching" or prevulcanization. The rapid change of plasticity with temperature[2] for unvulcanized rubber compounds increases the importance of temperature control since the temperature of the rubber determines the magnitude of the shearing forces which break up and disperse the masses of very fine pigment in the rubber.

It is interesting to notice that the process of "warming-up" rubber compounds by a short working of the cold stock on an ordinary two-roll mill, preparatory to further processing such as extruding or calendering, is the only one in which the low thermal conductivity of rubber is an

[2] Karrer, Dieterich and Davies, Ind. Eng. Chem. Anal. Ed. **2**, 96 (1930).

advantage. Since the required heat is generated by internal friction throughout the rubber mass, low conductivity is an advantage rather than a disadvantage since it makes surface cooling effects so small. Heating which would ordinarily require hours by conduction and radiation may be done in five minutes by working the rubber on a mill.

In a typical mill cooling test the average gross power input to the mill-line motor was about 150 hp for a mixing cycle which turned out four

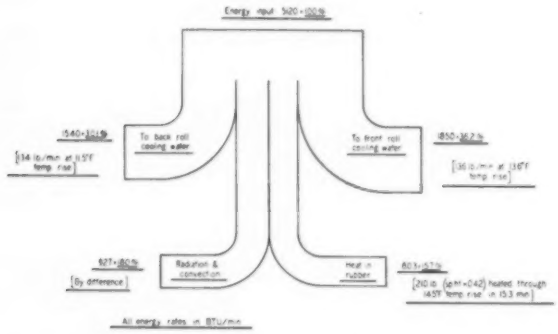

FIG. 1. Heat balance for a rubber mixing mill.

210-lb. batches per hour. After deduction of losses in the transmission system, motor, and mill bearings the net power input was about 121 hp—equivalent to a heat energy rate of 5120 B.t.u./min. The distribution of this energy is shown graphically in Fig. 1 in the form of a heat balance diagram. The losses were about 66 percent to the cooling water as measured by timed water-meter readings and differential multithermocouples, 16 percent in the form of sensible heat in the rubber in excess of the initial heat in the materials of the batch, as measured by a needle thermocouple, and, by difference, 18 percent in radiation, convection, and unaccounted-for losses. The total power input would have been sufficient to raise the temperature of the batch to nearly 1000°F, if that were possible without decomposing the rubber.

IV. Curing Problems

The process of vulcanization, in common with many other slow physico-chemical reactions, has a high temperature coefficient. The rate of vulcanization doubles for each rise of about 10 centigrade degrees.[3] This rate of increase varies with the composition of the mixture and with the choice of accelerators; and, particularly in the case of modern delayed-action accelerators, may vary considerably with temperature and time. However, for preliminary analysis it is convenient to make use of this approximate relation between temperature and rate of vulcanization. Variable temperature cures are sometimes evaluated on a more exact basis after determining by test the temperature coefficient of vulcanization for the particular rubber compound—using T-50 tests,[4] combined sulfur analysis, modulus, or other criteria of the degree of vulcanization obtained through a range of times at various temperatures.

Typical time-temperature relations for the ends and center of a long sheet of a "pure gum" rubber compound wrapped with thin wet cloth liner on an open metal drum and vulcanized in water are given in Fig. 2. Because of the thickness of the wrapped assembly, about 1", it was necessary in this experimental cure to combine several methods for reducing the variation in total vulcanizing effect along the sheet. A long slow "rise" (A) was used instead of a suddenly impressed maximum temperature. This was followed by a 15-minute "hold" at 285°F (B). At the proper time the heater was blown down by rapid release of pressure to equalize center and surface temperatures (C). This reduction of pressure permits removal of heat from the rubber by evaporation of part of the water in the wet interlining cloth, so that at the end of about 2 minutes the whole mass has attained a temperature of 280°F corresponding to the vapor pressure existing in the heater at that time (about 40 psi gauge). The cure was then continued at constant pressure and temperature for an additional period of 20 minutes from the beginning of the "blow-down" (D). Controlled slow, rather than rapid, final cooling was employed for 20 minutes (E) and the retention of heat in the inner plies was assured by maintaining a constant total pressure of air and steam during the cooling period to prevent evaporation and consequent cooling of the water in the wet liner. At the end of this cooling period the heater was finally blown down

[3] W. S. Coe and R. H. Gerke, Ind. Eng. Chem. **31**, 1478 and 1481 (1939).

[4] Gibbons, Gerke and Tingey, Ind. Eng. Chem. Anal. Ed. **5**, 279 (1933).

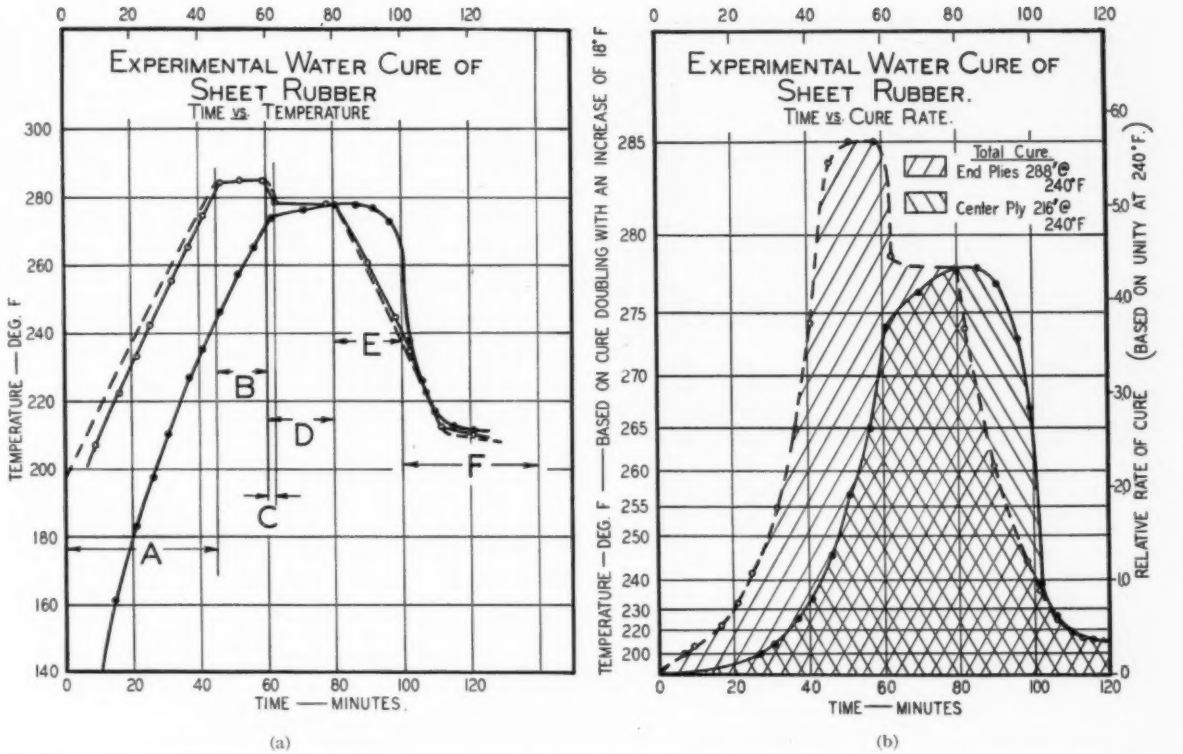

FIG. 2. (a) Time-temperature relations in water cure of sheet rubber. (b) Time-vulcanization rate relations for cure of Fig. 2(a). Areas under curves represent total vulcanization effects.

rapidly to atmospheric pressure (F) and the corresponding temperature (210°F).

Temperatures as determined by the use of waterproof thermocouple equipment in this cure are shown in the figure on two different bases of comparison. At the left, in Fig. 2(a), is shown the normal time-temperature relation, while 2(b) shows the relation between vulcanization rate and time, using for convenience a special temperature scale based on the assumed doubling of rate of vulcanization in each 18°F interval. Since degree of vulcanization = vulcanizing rate × time, areas under the curves in 2(b) are proportional to total amount of vulcanization. It may be seen that, while the total equivalent effect for the ends of the sheet was that which might be attained in 288 minutes at 240°F, the total for the center was 216 minutes at 240°F, or 75 percent as much. The variation in this unusually long sheet would, of course, have been much greater had more ordinary methods of vulcanization been employed. For instance, the total equivalent vulcanization for the center ply was increased 17 percent by the use of the special pressure cooling technique over that which would have been obtained with ordinary "blowdown" cooling.

The enormous advantage in time saving to be gained by application of heat to both sides of a thick rubber article may be illustrated by the comparison of an internal heat cure of a large pneumatic truck tire with another cure of the same tire with no internal heat. The internal heat cure was pioneered in this country by the B. F. Goodrich Company with the advent of the cord tire about twenty years ago. It is based on an initial application of saturated steam at about 340°F and 100 psi gauge to the thick-walled rubber water bag which expands against the interior surface of the tire, followed by a much longer holding period during which the bag temperature is held nearly constant by hot water under sufficient pressure to force into the cord structure some of the surrounding rubber and to knit the whole mass together into the form imposed by the external mold. Proper choice of times and temperatures avoids the necessity of circulation of the hot water used in the main part

FIG. 3. Cross section of tire and water bag in steel mold showing locations of thermocouples.

of the cure, although water is circulated in special cases. External heat is applied according to a prearranged schedule of time and temperature starting at a definite time after the initiation of internal heat.

A typical tire cross section with associated water bag and curing mold is shown in Fig. 3. On the tire section are shown the locations of the thermocouples used to secure the curves in Figs. 4 and 5, which present a comparison of an air bag cure without internal heating and a water bag cure as described above.

The wide difference in uniformity of vulcanization obtained by the two processes is evident. Only by the use in different parts of the tire of compounds curing at four or more different rates could the air bag cure produce results approaching the uniformity obtained in the water bag cure. The difference in vulcanization by these methods is naturally much less in thinner tires such as those used in passenger-car service.

Surface heat transfer rates in open steam and most mold cures are so high in comparison with the low thermal diffusivity of rubber compounds that they may be considered to be infinite. For that reason time-temperature relations in many objects of simple form can be predicted with considerable accuracy. There are, however, some other vulcanization processes in which the heat transfer rates are neither high nor uniform. In these, air, steam-air mixtures of changing composition, or water may be used as the heat transfer medium for a variety of reasons.

Typical time-temperature relations for a portion of an air pressure cure of footwear are shown in Fig. 6. Here the initial air temperature of about 210°F was increased during the one-hour rise portion to 250°F and then held at that temperature for 1½ hours. Pressure was 30 psi gauge during the first two hours and atmospheric thereafter. The pressure serves to make the rubber-fabric structure of the shoes more compact and to increase the surface heat transfer rate. Radiation and forced convection were chiefly responsible for transfer of heat to the goods. Air temperatures at two representative points in a vulcanizer holding about 4000 pairs of shoes, and the temperature of parts of two typical shoes, are shown. The test from which these data were taken was one of several which indicated that uniformity of convection and radiation heating were the most important factors in obtaining uniform vulcanization throughout the vulcanizer. It was proved that measurement of temperatures in the goods was unnecessary if enough air thermocouples were employed to give a complete picture of the distribution of heat in time and space. This study is typical of many which are not amenable to theoretical analysis.

V. Product Problems

Many rubber products, particularly those built up of rubber and fabric, are subject in service to rapid cyclic stresses with the inevitable conversion

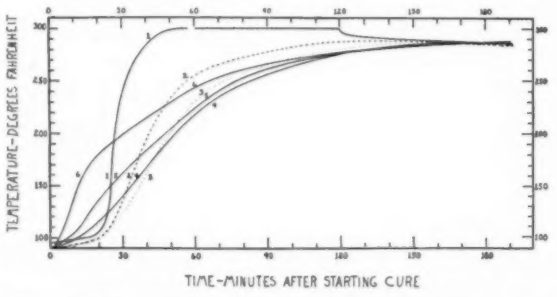

FIG. 4. Temperatures in a tire during an "internal heat" cure, heat being supplied from both sides. Couples are located as follows: No. 1, at surface of tread next to mold; No. 2, at base of tread; No. 3, at top of 12th ply; No. 4, at top of 8th ply; No. 5, at top of 4th ply; No. 6, at surface of inner (1st) ply next to water bag.

of some of the energy input into sensible heat. One of the most important problems of the designer and compounder is that of reducing the amount of heat generated by hysteresis to the

lowest value economically practical, and of designing for the best possible dissipation of that unavoidably produced. Continuous high speed operation of modern, heavy-duty motor vehicles under severe road and temperature conditions has made the reduction of temperature due to internal losses in tires one of the most important single problems in tire design.

The measurement of tire temperatures under road and laboratory test conditions is an important aid to the tire designer in evaluating the effects of changes in compounds and constructions. So far as is known, no method of measuring temperatures accurately in a moving tire has ever been put into common practice. The rise in air pressure in a tire from cold to running conditions has been used as a crude gas thermometer measurement of average temperature but this method is subject to serious errors because of thermal expansion and plastic growth in the tire structure, and diffusion of air through the wall of the inner tube. Moreover, knowledge of an approximate average temperature is not nearly so

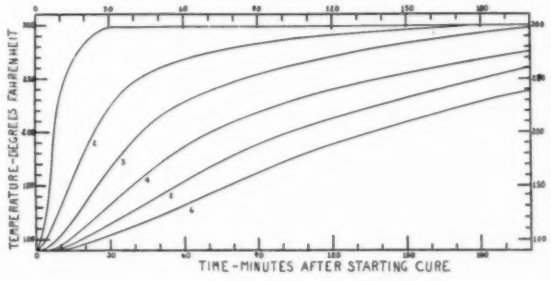

FIG. 5. Temperatures in a tire during an "air bag" cure, heat being applied from outside only. Couple locations, bag and mold are same as for Fig. 4.

important as knowing with considerable exactness the temperature and location of the hottest part of the tire. Measurements of this type have been made with fine wire thermocouples inserted with a tool to accurately known depths in selected parts of a tire which has just been stopped. After observing temperatures over a period of several minutes at known time intervals beyond the instant of stopping the tire, the observer may calculate by extrapolation the maximum, under operating conditions, at the point occupied by the thermojunction. Such measurements show maximum internal temperatures in large tires run at high speeds with normal load and inflation

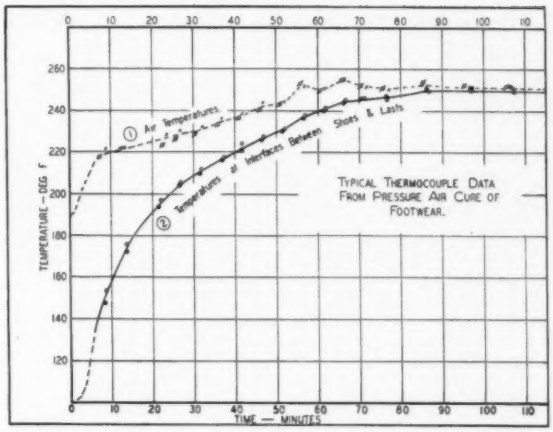
TEMPERATURE - DEG F
TIME — MINUTES
① Air Temperatures
② Temperatures at Interfaces Between Shoes & Lasts
TYPICAL THERMOCOUPLE DATA FROM PRESSURE AIR CURE OF FOOTWEAR.

FIG. 6. Thermocouple data from pressure air cure of footwear.

pressure to be over 210°F, approaching vulcanization temperatures. Yet the truck or bus owner knows that such tires will render well over 1000 hours of uninterrupted service at speeds of 20 to 60 miles per hour or more.

The thickness of a tire structure must be made as small as practical design will permit unless the tire is to be used exclusively in low speed service. Each increment of thickness not only adds resistance to the flow of heat from all inner layers, raising their temperatures, but it makes its own contribution to the heat which must be dissipated from the surface. Thus the maximum temperature in a tire structure increases very rapidly with increasing thickness. In a number of cases the service of thinner, apparently weaker, tires has exceeded that of standard heavy gauge tires in high speed service because the running temperatures of the thinner tires were lower.

In many applications of *V*-belts, their life is determined to a considerable degree by their internal operating temperature. The conditions in one acceptance test for *V*-belts were so severe that some belts failed in a few minutes through heat blowout, literally through pyrolysis of the organic materials in the rubber compounds, and charring of the cotton. Belts of that particular construction were nevertheless known to last several years in ordinary service. Concentrated attack on the problems of compounding and construction finally produced a belt of the same size which ran sufficiently cooler to have a life of 64 hours under the same test conditions, an increase in life of about a thousand-fold.

The extreme temperatures which may be developed in rubber products subject to cyclic stress are illustrated also by the occurrence of heat blowouts in solid tires when they were in common use on motor trucks. Breakdown of the rubber at the thermal center of the tire section, resulting from temperatures of over 500°F, caused the generation of gases under sufficient pressure to burst the overlying layers of rubber. Thermal failures of another type were observed in experimental work on a hydraulic device which used rubber-covered parts as valves to control cold water at high pressure. A jet of high pressure water, $\frac{1}{4}''$ in diameter, impinging on a layer of rubber, $\frac{1}{4}''$ thick, which was bonded to metal, produced heat blowouts in the rubber. These failures occurred in a few minutes even when the sample was immersed in water at 40°F under a jet at the same temperature.

Heat transfer problems are of importance occasionally in the design of rubber-lined chemical-processing equipment. The temperatures of reaction vessels may be controlled by means of water jackets or by coils. These heat-transfer surfaces may be covered with rubber for protection against chemical attack. In a typical case of this character a water solution at 160°F in a rubber-lined reaction vessel was to be cooled by means of a surrounding water jacket. Rubber $\frac{1}{8}''$ thick, having a conductivity of 1.2 B.t.u./(hr.)(ft.)^2(°F/in.), was to be used to line the vessel. The cooling water had a mean temperature of 80°F. The circulation conditions inside and outside the tank indicated that the heat transfer coefficient at either wetted surface was about 300 B.t.u./(hr.)(ft.)^2(°F). The vessel walls were made of $\frac{1}{4}''$ thick steel.

The total thermal resistance, R, of such a wall will be equal to the sum of the resistances of the two water films, the rubber, and the steel: or $R=1/h_s+1/k_r/t_r+1/k_s/t_s+1/h_s$, in which h_s = surface heat transfer coefficient, k_r = thermal conductivity of rubber, t_r = thickness of rubber, k_s = thermal conductivity of steel, and t_s = thickness of steel.

$$R=1/300+1/1.2/\tfrac{1}{8}+1/312/\tfrac{1}{4}+1/300$$
$$=0.003+0.104+0.0008+0.003$$
$$=0.1108\ [(\text{B.t.u.})/(\text{hr.})(\text{ft.})^2(°\text{F})]^{-1}$$

or the over-all heat transfer coefficient = 1/0.1108 = 9.0 B.t.u./(hr.)(ft.)^2(°F).

Thus, it may be seen that the thermal resistance of the $\frac{1}{8}''$ thickness of rubber is about 95 percent of the total. The thermal resistance of the water films is negligible in comparison. This is not true, of course, in the case of a bare metal reaction vessel where the water films would have offered approximately 88 percent of the total

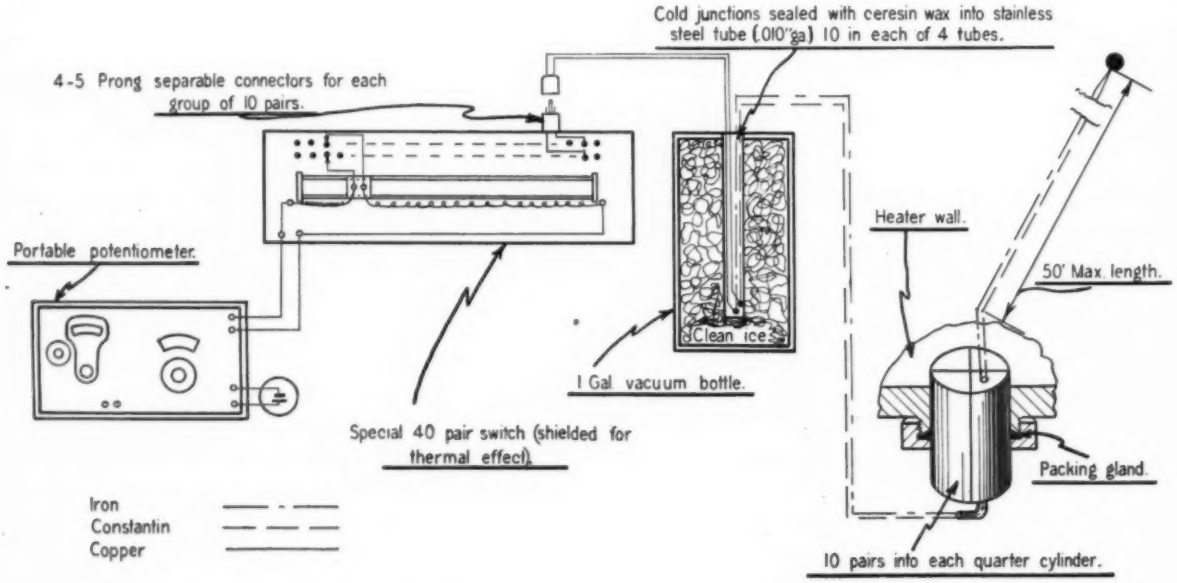
Cold junctions sealed with ceresin wax into stainless steel tube (.010"ga) 10 in each of 4 tubes.
4-5 Prong separable connectors for each group of 10 pairs.
Portable potentiometer.
Heater wall.
50' Max. length.
Clean ice
1 Gal vacuum bottle.
Special 40 pair switch (shielded for thermal effect).
Packing gland.
Iron
Constantin
Copper
10 pairs into each quarter cylinder.

FIG. 7. Typical circuit in thermocouple set for testing air vulcanizers.

resistance. However, it is unfair to compare rubber-lined with bare metal equipment of the same metal composition and thickness. In many cases no metal would serve the purpose, and in most cases any special chemical-resistant alloy would be much thicker and would have a considerably lower thermal conductivity than the thin steel normally used for rubber-lined chemical vessels.

VI. Thermocouple and Other Heat Measurements

A discussion of the thermocouple technique used in the rubber industry is necessarily beyond the scope of this paper. A few examples of the type of equipment and circuits used are, however, mentioned to illustrate general design features. Figure 7 shows a typical circuit in a 40-point thermocouple set of iron-constantan wire designed for use in an air heater 8 ft. in diameter ×40 ft. long in which footwear is vulcanized. Note that each circuit is made up of one pair of thermocouple wires continuous from hot junction to cold junction and that switching is done only in the copper leads between cold junctions and potentiometer binding posts in order to eliminate thermoelectric effects in the switch.

Because of the necessity for accommodating testing technique to the tempo of factory operations, the thermocouples are installed in the cars of footwear before they are rolled into the heater. Four cables, each containing ten circuits made up of leads, cold junctions and a packing gland adapter, are arranged for convenient insertion through a single air-tight packing in the heater wall. Connection between cold junctions and leads is made by means of multicircuit connectors. Readings are taken manually at the rate of about ten per minute with a portable potentiometer. This equipment illustrates the semicommercial adaptation of well-known laboratory methods. The design is based on two main requirements: (a) elimination of all possible thermoelectric effects in spite of severe temperature gradients inside and out of the heater and considerable heat radiation on lead wires and instruments; (b) speed of operation required by the necessity of making test heats as nearly like production heats as possible and by the fact that frequent readings at each of a large number of points had to be obtained in order to study rapidly fluctuating air temperatures. The curves of Fig. 6 are representative of data taken with this equipment.

FIG. 8. Thermocouple equipment in use in a study of tire cures in heater press equipment.

In Fig. 8 is shown the type of equipment used in the study of tire and other steam and water cures. Inside the open heater-press may be seen the uppermost of a stack of tire molds which contains a tire made with built-in thermocouples. These are made of ordinary base-metal thermocouple wire which has been covered with a rubber compound capable of withstanding long exposure to steam at curing temperatures. The wires are brought out through a junction box and packing gland as continuous lengths to an iced cold junction bottle from which the circuits continue through copper leads to a switch shielded to avoid thermal gradients as much as possible, and finally to a portable hand potentiometer.

The importance of avoiding thermoelectric errors in low voltage thermocouple circuits cannot be overemphasized. Thermocouple equipment subject to many such sources of error sometimes is found in otherwise well regulated laboratories. Casual drafts and stray heat radiation often have been observed to cause errors of as much as 0.15 mv in circuits designed to measure about 300°F maximum (about 8 mv). In low range thermoelectric equipment, it is always best to avoid all discontinuities in the thermocouple wires, even though connections are soldered. Automatic or manually controlled cold junction compensators are to be avoided unless the temperature at the cold junction can be

measured accurately and prevented from drifting rapidly so that a voltage differential between the two sides of the circuit may be set up. Carefully made cold junctions in clean ice kept in pint or quart vacuum bottles are recommended. Commercially available portable equipment can be relied upon to give results accurate to better than ± 0.5°F if it is used carefully and all sources of thermal and calibration error are avoided. The rubber industry as a whole is possibly the largest user of equipment of this type in ranges up to 400°F.

The remarks about compensators do not apply to the several excellent commercial automatic potentiometer type temperature recorders which have built-in cold junction compensators of the nickel resistance-bridge or other type. Instruments of this kind, although usually installed permanently for recording or controlling operations, may sometimes be found suitable for test work. Usually, however, they are not adapted to rapid recording of more than two points and cannot be set up conveniently and quickly enough.

Some use is made of direct-reading thermocouple pyrometers, especially in the measurement of temperatures of mill and calender rolls and of crude and compounded rubber. In measurements of the former type the hot junction is formed at the center of a band of the thermocouple alloys, which is held in sliding contact under light pressure against the moving metal surface of the roll by a hand-held frame. Rubber stock temperatures are read by using a separate hand-held thermocouple which is protected by a small stainless steel hypodermic needle. The direct reading instrument is a sensitive microammeter equipped with a bimetallic cold junction compensator. These instruments must be carefully checked for calibration errors, transient thermal effects and balance errors. However, the convenience of the hand-held, direct-reading instrument often outweighs its somewhat limited accuracy.

VII. Summary

The threefold heat problems of the industry are, in order of their occurrence: (1) Controlled removal of heat generated in processing crude rubber. (2) Regulation of heating and cooling processes to give the most nearly uniform vulcanization in the shortest possible time. (3) Measurement and reduction of heat generation in products subject in service to cyclic stress conditions.

Each of the three types of problems engages the attention of chemists and engineers as well as physicists. The chemist is constantly searching for new ingredients and combinations of materials which will promote rapid vulcanization at curing temperatures, that is, 240 to 320°F. The same rubber compounds, when unvulcanized, must be relatively insensitive to processing temperatures up to about 220°F; when vulcanized they must withstand prolonged use at temperatures above 200°F. The engineer must design curing equipment and related automatic controls. He also must design the combinations of rubber compounds and structural elements which make up the products of the industry. The physicist must measure and analyze the thermal properties of the raw materials, the rubber compounds and the finished products. He also must apply the methods of the physics laboratory to the study in the factory of thermal problems connected with production operations. The cooperation of all is essential in producing for the consumer better products at lower cost.

Dielectric Constant and Power Factor of Certain Kinds of "Koroseal" at Radiofrequencies

BY OMER R. FOUTS

Department of Physics, University of Akron, Akron, Ohio

IN the last few years great progress has been made in the development of rubber substitutes. Among such rubber substitutes is a group of elastoplastics commonly known as "Koroseal." This group consists essentially of polyvinyl chloride mixed with certain other substances which serve as plasticizers. For certain electrical applications the plasticizer consists of tricresyl phosphate of varying proportions depending on the plasticity desired. Also, a small amount of lead oxide is sometimes added.

Fuoss[1] has made a careful investigation of the effect of frequency and temperature on the power factor and dielectric constant of such compounds over the frequency range 20 to 10,000 cycles per second. He reports that the dielectric constant varies with frequency and temperature between the limits of 3 and 10, and even greater variations in the power factor. Also Davies and Busse[2] have reported some measurements on the dielectric properties of plasticized polyvinyl chloride in the commercial and audiofrequency range. It is therefore of interest to report a few measurements of the dielectric constant and power factor of such compounds at higher frequencies in the range 100 to 2400 kilocycles per second.

The method used was an old and very simple one commonly called the "resonant substitution method." It consists of the direct substitution in a resonant circuit of a known variable air condenser with a known resistance in series, in place of an imperfect condenser having the test sample as the dielectric. The use of a sensitive vacuum tube voltmeter instead of the usual hot wire galvanometer for determining the exact resonant condition is a great improvement. See Fig. 1. O is a simple Hartley oscillator of variable frequency; L is a variable self-inductance; C_x is a condenser having test sample as dielectric; C_s, a known variable air condenser; R, a known high frequency resistance box; and V a sensitive vacuum tube voltmeter.

Observations were made in this manner. The frequency of the oscillator and the inductance L (with C_x in series) were adjusted to resonance and the voltmeter reading noted. Then C_s and R were substituted in place of C_x and the exact resonance obtained by varying C_s. Then R was increased until the voltmeter reading was reduced to the same value as before.

The vacuum tube voltmeter used was a very sensitive one of the slide back type described by Reich.[3] It utilizes a type 22 tube with screen grid

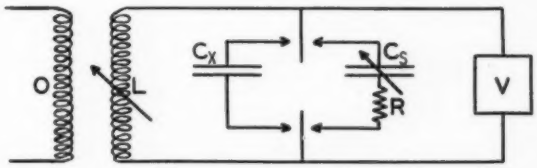

FIG. 1. Circuit for the measurement of dielectric constant and power factor.

used as the control grid. All frequencies were measured with an absorption type wave meter. Circular tin foil sheets having diameters approximately 12.5 cm and 15.0 cm were used as electrodes. No guard ring could be used but an attempt was made in some cases to correct for the edge effect in the manner described by Hoch.[4]

The dielectric constant and the power factor were computed from the well-known relations

$$\text{Dielectric constant} = \frac{C_x}{C_v}$$

$$\text{Power factor} = 2\pi f R C_x$$

where, C_x = measured value of the capacitance,

[1] R. M. Fuoss, J. Am. Chem. Soc. **61**, 2334–2341 (1939).
[2] Davies and Busse, "Dielectric properties of plasticized polyvinyl chloride," Report before the 99th meeting Am. Chem. Soc. at Cincinnati, April, 1940.
[3] Reich, Electronics **3**, 109 (Sept., 1931).
[4] Hoch, Bell Sys. Tech. J. **5**, 555 (1926).

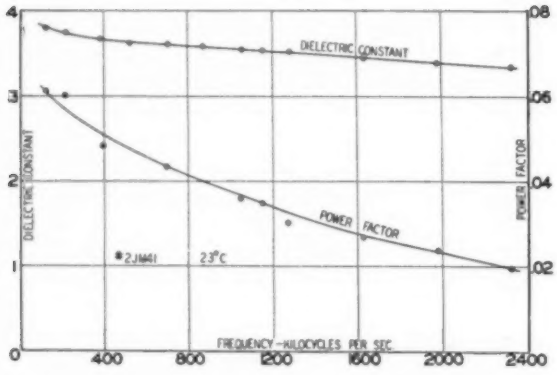

FIG. 2. Data for a typical compound.

C_v = calculated value of capacitance assuming vacuum as dielectric, R = equivalent resistance of condenser C_x, f = frequency in cycles per second.

No claim is made for a high degree of accuracy, the measured values of the dielectric constant may be in error by as much as 2 or 3 percent and the power factor as much as 5 or 6 percent.

Seven samples of polyvinyl chloride plasticized with tricresyl phosphate were tested, these having compositions as shown in Table I.

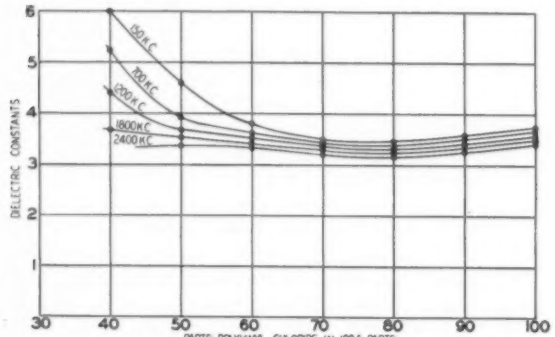

FIG. 3. Dielectric constant *vs.* composition.

The data for a typical compound is shown in Fig. 2. A complete analysis of all results obtained from the seven samples is shown in Figs. 3 and 4.

TABLE I.

SAMPLE NO.	P. V. C.	T. C. P.	PbO
2 JM 37	100	0	0.5
2 JM 38	90	10	0.5
2 JM 39	80	20	0.5
2 JM 40	70	30	0.5
2 JM 41	60	40	0.5
2 JM 42	50	50	0.5
2 JM 43	40	60	0.5

Conclusions

(1) In the frequency range 100 to 2400 kilocycles the dielectric constant of these compounds varies from 3.5 to 6 with a minimum when the amount of plasticizer present is about 25 parts in 100.5.

(2) In the same frequency range the power factor varies from 0.17 to 0.01 with a minimum when the amount of plasticizer present is about 20 parts in 100.5. All measurements reported here were made at room temperature, approximately 23°C.

The test samples used were obtained through the kindness of Mr. Davies and Dr. Busse of the B. F. Goodrich Rubber Company. Actual experimental data were taken by Mr. Charles Hoskins and in part checked by other observers.

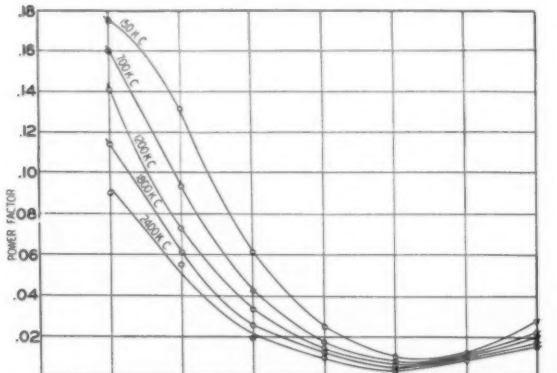

FIG. 4. Power factor *vs.* composition.

An X-Ray Study of the Proportion of Crystalline and Amorphous Components in Stretched Rubber

By J. E. Field

The Goodyear Tire and Rubber Company, Akron, Ohio

A method is described for obtaining a quantitative measure of crystalline hydrocarbon present in stretched rubber samples by comparing the intensities of the diffraction spots and the amorphous halo appearing in the x-ray diagrams. This method has been applied in studying the crystallinity of stretched vulcanized rubber as it is affected by different vulcanization accelerators, and variations in extension, temperature and cure. To illustrate a connection between the physical performance of a rubber vulcanizate and its degree of crystallization, measurements were made on the relation of crystallinity to creep when the rubber was stretched to different initial elongations under constant loads. The creep as a function of the elongation has a maximum value at the same intermediate elongation for which crystallization becomes appreciable. At higher elongations, the increased crystallinity results in a diminution of the creep. The ultimate strength and extensibility generally associated with stretched vulcanized rubber is the result of the combined effect of the primary valence cross-linkages formed by vulcanization and the formation of crystallites caused by stretching. Crystallization is an important factor in maintaining the relatively high strengths of vulcanizates having a greater range of extensibilities. In general, the physical properties and performance of vulcanized rubber is related to the amount of crystalline material formed upon stretching, which of course depends upon the structural characteristics of the vulcanizate.

Introduction

UNDER ordinary circumstances, the x-ray diffraction pattern of rubber is similar to that of a liquid displaying an amorphous structure.[1] However, under limited conditions of stretching[2–4] or freezing,[5, 6] rubber exhibits a crystalline phase of its structure in that the x-ray diagram indicates the appearance of crystallites which, in the case of stretching, are aligned along the axis of stretch. Typical diffraction patterns for unstretched and stretched rubber are shown in Figs. 1 and 2. Although the mechanism of this transition is not yet fully understood, it resembles in many respects the crystallization of a supercooled liquid.[7] In the early investigations of Katz,[4] and Hauser and Mark,[8] it was learned that the fiber diagram made its appearance only after a minimum elongation had been reached and, as stretching proceeded, the intensity of the diffraction spots increased and the intensity of the halo decreased. The elongation at which the spots attain an appreciable intensity is usually in the range 150 percent to 275 percent, depending largely upon the sample and the conditions of stretching and the temperature. The x-ray diffraction phenomena for rubber have been covered in a recent review article which includes a bibliography on the subject.[9]

Even in highly stretched rubber a faint halo persists, indicating the presence of some amorphous material. Meyer and Mark[10] estimated that at least 80 percent of very highly stretched rubber is crystalline. The formation of crystallites is very noticeably influenced by the temperature. Thiessen and Wittstadt[11, 12] have shown that an equilibrium condition is attained for the crystallization depending upon the elongation, temperature and pressure. According to the fusion curve of Susich,[13] for stretched raw rubber, only amorphous x-ray diagrams appear above a temperature of 90°C.

It is reasonable to expect that the physical properties of rubber will be influenced to a large extent by the coexistence of the amorphous and crystalline hydrocarbon in various proportions. Experiments with unvulcanized rubber have already shown this. Thus, Hintenberger and Neumann[14] found that in the case of raw rubber a maximum elongation appeared at relatively

FIG. 1. Unstretched rubber.

small stresses when the elongations were plotted as a function of the constant loads applied over a fixed period of time. Also, a critical range of loadings was found within which the probability of rupture of the rubber samples was greatest. This maximum became more pronounced with increase in temperature and its occurrence was explained as a combined effect of flow and crystallization, the latter beginning to occur in this critical region. Later, Hauk and Neumann[15] extended the investigation to vulcanized compounds, with similar results. Braun[16] found that samples of stretched vulcanized rubber tended to fail at intermediate elongations when stretched for a long period of time. A maximum dynamic fatigue life at relatively low stresses also has been demonstrated.[17]

The effect of vulcanization on the x-ray diagram was investigated by Katz and Bing.[18] Using a much higher sulfur content than is required in modern compounding, they found that higher elongations were necessary for the appearance of the fiber diagram as the vulcanization progressed. Since milled raw rubber does not give a fiber diagram under normal conditions, it is reasonable to believe that vulcanization assists crystallization by means of molecular immobilization until the rigidity introduced by the network of primary valence cross-linkages begins to prevent the movement of the molecules into the crystal lattice.[9]

The basis of modern rubber technology lies in the ability to vulcanize rubber with a wide range of physical properties, thus making possible its adaptation for any particular condition of service. This result is secured by the use of an extensive array of compounding ingredients, including pigments, softeners, etc., but more particularly by the selection of suitable accelerators or chemical agents which promote vulcanization. This work was concerned with measurements of the relative proportion of crystalline and amorphous material in typical stretched vulcanizates in an effort to find some connection here with the physical properties.

Experimental Procedure

A General Electric x-ray diffraction unit, equipped with a Kenotron rectifier and General Electric copper anode tube, was used to obtain the diffraction patterns. The tube was operated at 35 kv potential and 25 ma. For the majority of the patterns, the Cu$K\beta$ radiation was filtered out by means of a nickel foil. A nonrecording microphotometer was used to measure photographic densities.

In order to carry out experiments on stretched rubber above room temperature, an especially

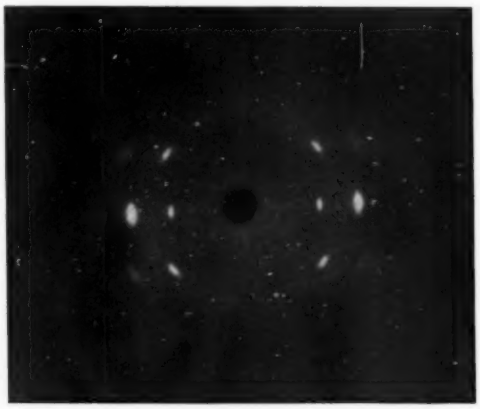

Fig. 2. Stretched rubber.

designed thermostat was used. This consisted of a jacketed copper block around which oil was circulated by means of a gear pump. The oil was maintained at a constant temperature by flowing through a copper spiral immersed in a constant temperature bath. The temperature of the sample was measured by means of a thermocouple. In order to permit the passage of the x-ray beam, the block was provided with windows which were covered with Cellophane. A sketch of the arrangement is shown in Fig. 3.

It is known that the intensity of the diffraction for vulcanized rubber depends to some extent on the stretching procedure, and, in fact, a hysteresis effect for the crystallization has been demonstrated by Iguchi and Schossberger[19] and by Clark.[20] In this work, a standard procedure for stretching was adopted. Strips of vulcanized rubber were cut from 2-mm gauge test sheets by means of a die. These were stretched in a uniform manner by means of a falling weight, the desired elongation being obtained on the initial stretch by adjusting the distance through which the weight falls. The same procedure was used for stretching strips of raw rubber which were cut from uniform sheets of evaporated latex. Several gauges of the latter were used to determine the effect on the measured crystallinity. A micrometer dial gauge was used to determine the thickness of the rubber samples.

It has been pointed out that the amorphous and crystalline phases of stretched rubber exist simultaneously and, as stretching proceeds, the intensity of the diffraction spots increase while the intensity of the halo decreases. This relationship offers a possibility to calculate the relative amount of crystallinity in stretched rubber by matching the intensity of the halo with that produced by an unstretched sample of reduced thickness. In order to make this calculation, the intensity of the halo as a function of the thickness of the unstretched rubber must be known. This is shown in Fig. 4. The conditions of exposure and development for these patterns were carefully controlled and corrections were made for any variation in tube out-put by means of a control spot from the incident beam which was simultaneously exposed on the film through a thin lead strip. The operation of the tube was so steady, that with ordinary precautions in exposure and development, patterns were obtained which required at most only small corrections, as ascertained by variations in the density of the control spot. It is realized that the radiation producing the control spots was harder than the Cu$K\alpha$ radiation producing the pattern because of the filtering action of the lead, but this effect was minimized because any corrections based on the control spots were so small.

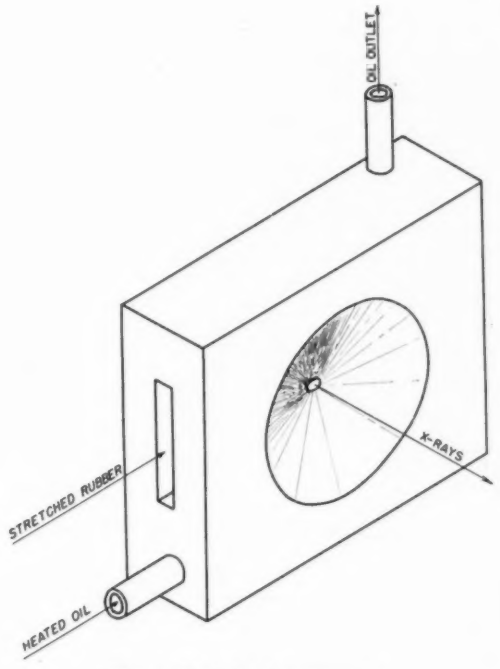

Fig. 3. Sketch of thermostat.

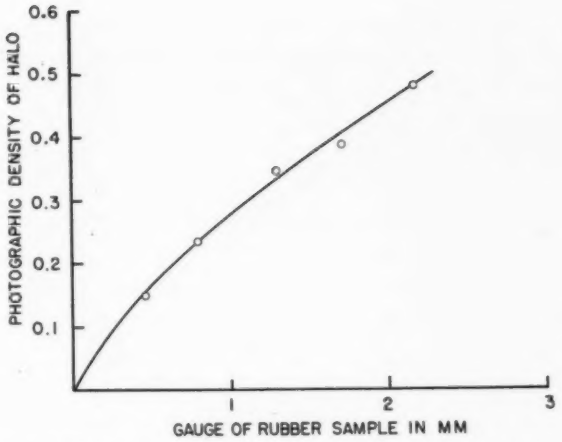

FIG. 4. Halo intensity for unstretched, unvulcanized rubber.

The proportion of crystalline material at any given elongation may be calculated by referring to the relationship shown in Fig. 4. Because of crystallization resulting from stretching, the intensity of the halo for a stretched sample will be less than that for an unstretched sample of the same thickness. From the measured intensity of the halo for a stretched sample, it is possible to obtain from Fig. 4 the effective thickness of the amorphous material remaining in the sample, and the difference between this and the actual gauge represents the amount of crystallized

material. Thus, if X_0 is the measured gauge of a stretched rubber sample at any given elongation and X is the effective thickness of amorphous material, the percent crystalline material may be calculated by means of the formula,

$$\% \text{ crystalline material} = \frac{100(X_0 - X)}{X_0}.$$

It should be noted that only the intensity of the halo was considered in the derivation of the above formula, the diffraction spots receiving no consideration.

Since the crystalline material is formed upon stretching at the expense of the amorphous

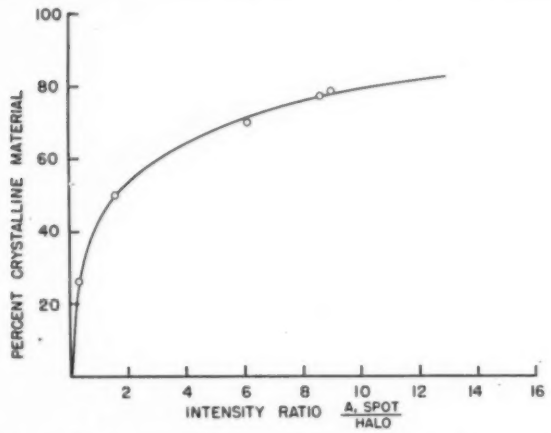

FIG. 5. Compositions indicated by intensity ratios in the patterns.

phase, it is evident that the ratio of the intensity of the A_1 diffraction spot to the intensity of the halo is a measure of the crystallinity. This has the advantage of being independent of all exposure factors. The relation between this ratio and the percent crystallinity, shown in Fig. 5, was obtained from measurements of patterns which were carefully controlled in the manner previously described together with the application of the above formula to these same patterns. Once this relation is carefully established, the percent crystallinity may be readily obtained for a given spot-halo ratio regardless of exposure conditions. This calibration curve, so to speak, was applied to the vulcanized gum stocks used in this work to determine the crystallinity under various conditions.

On all the films for vulcanized rubber, the quantities measured were the densities of the A_1 spot and the halo. A uniform procedure was followed in obtaining halo densities. Density values were secured across a diameter of the halo. These were plotted, a back-ground density determined from this curve and the maximum density above this taken as the density of the halo.

Experimental Results

CRYSTALLINITY OF STRETCHED RAW RUBBER

X-ray diffraction patterns were recorded for samples of evaporated latex sheets at elongations ranging from 250 percent to 700 percent under two different conditions. In the one case, the gauge of the sample was 2 mm before stretching, the final gauge therefore varying according to the degree of stretch. In the other case, the initial gauge was so adjusted that the gauge after stretching was always 0.25 mm. The relative proportions of crystalline and amorphous material present, when samples were stretched according to the above conditions, is comparable as shown in Fig. 6, so that in the work which follows, the experimental procedure was simplified by using samples of the same initial

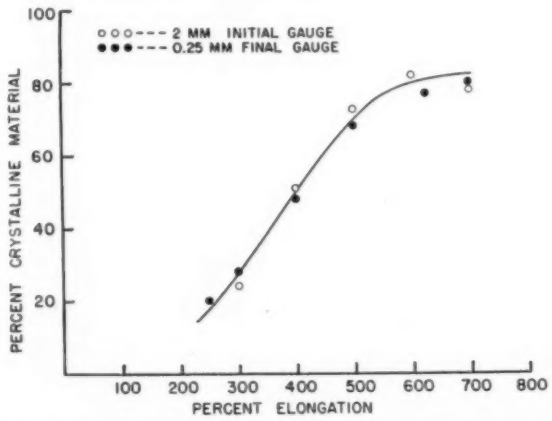

FIG. 6. Crystallization of stretched, unvulcanized rubber.

gauge. These curves, by extrapolation, indicate that the crystallization has advanced far enough to become evident in the neighborhood of 175 percent elongation. At the start, the curves are practically linear, but approach asymptotically a value of about 80 percent at the higher elongations. This implies that the maximum amount of crystalline material created by stretching is about 80 percent of the total rubber. It is probable that

the crystalline proportion would be slightly greater than this if consideration is given to the impurities in the latex which tend to increase the intensity of the halo. It would be difficult to check this result with the crystallization because of freezing because, in the latter case, Debye-Scherrer rings appear in the region of the halo, making intensity measurements of the halo too unreliable. Taking accepted values of 0.92 and 0.95 for the densities of amorphous and highly stretched rubber, respectively, a density of 0.965 for the crystalline rubber is deduced. This compares well with the highest measured value of the density obtained from rubber that had been stretched and frozen.

The crystallinity at various elongations of evaporated latex sheet was determined from x-ray diffraction patterns recorded at room temperature. Diagrams for these same samples were obtained at 90°C and again at room temperature at the same constant elongation and the effect upon the crystallinity was observed. These changes in crystallinity are shown in Fig. 7. The courses of the crystallization curves in the lower range were determined from the maximum elongations at which crystallization has not yet become evident.

According to one point of view[11] there is a statistical distribution of melting points over a

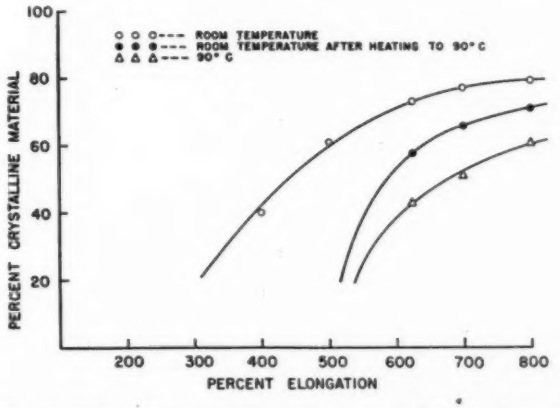

FIG. 7. Effect of temperature on the crystallinity of unvulcanized rubber.

temperature range, so that the decrease in crystallinity at the higher temperature would be attributed to the disappearance of crystallites whose melting points are 90°C or less. On the other hand, we may be dealing with a system which reaches an equilibrium analogous to that reached by a saturated solution in contact with the solid solute. Another factor to be considered in the lower amount of crystallinity at the higher temperature is the plastic flow. This accounts for the failure of the crystallinity to regain its original value at room temperature after the heating for 15 minutes at 90°C and re-exposed without retraction. The amount of plastic flow undoubtedly increases with the time of heating, thus making this effect more pronounced the longer the time of heating. Also, the plastic flow is reduced by the increased amount of crystallinity at the higher elongations. At the lower elongations, after the above heating, the plastic flow is sufficient to prevent any recrystallization of the clamped sample at room temperature. This is accompanied by a higher permanent set at the lower elongations.

TABLE I.

COMPOUND	*A*	*B*	*C*	*D*
Smoked sheet	100	100	100	100
Zinc oxide	1	2	1	3
Sulfur	3	2	2	5
Stearic acid	0.5			
Captax	0.5			
P.P.D.		2		
Zimate			1	
D.P.G.				1

CRYSTALLINITY IN STRETCHED VULCANIZED RUBBER

The formation of crystallites in vulcanized rubber is influenced to a very large extent by changes in internal structure brought about by the processing, by the action of the compounding ingredients and by the curing treatment. Since the greatest differences in crystallinity would be expected to be found between vulcanizates having a wide range of physical properties, x-ray diffraction patterns of the gum stocks shown in Table I were investigated under various conditions. The trade names of the accelerators used in compounding these stocks are listed below with their respective chemical names.

Captax	2-Mercaptobenzothiazol
Accelerator 552 (P.P.D.)	Piperdinium pentamethylene dithio carbamate
Zimate	Zinc dimethyldithio carbamate
D.P.G.	Diphenylguanidine

Hereafter, Accelerator 552 will be referred to as P.P.D. throughout this work. The range of physical properties for these vulcanizates is shown in Table II.

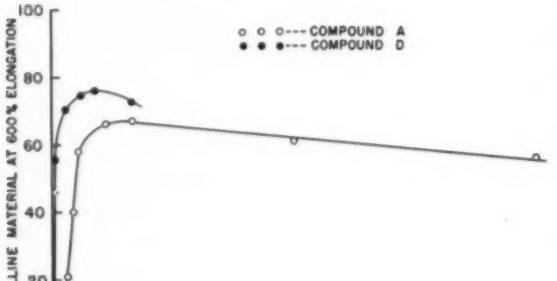

FIG. 8. Dependence of crystallinity on cure.

The effect of the time of cure on the crystallinity in compounds *A* and *D* is shown in Fig. 8. As the cure progresses, the crystallinity increases sharply to a maximum and then gradually decreases. The position of this maximum undoubtedly changes relative to the curing time for different compounds, as indicated by the curves for the two compounds shown here. In the early stages of the vulcanizing process, no crystallization upon stretching is apparent. However, crystallites are very readily formed when the uncured stock is frozen, as is evidenced by the appearance of the Debye-Scherrer rings in the x-ray pattern. This is understandable if it is considered that extending throughout the structure of the rubber there are more or less ordered regions which might be compared with the molecular clusters throughout a liquid which give rise to the halo in the diffraction pattern. These ordered regions become the nuclear centers from which crystallization proceeds when internal forces are set up by stretching or freezing. The extensive milling and processing in preparation for vulcanization apparently do not completely destroy these ordered regions, but they do increase the plasticity to the extent that the internal forces set up by stretching are insufficient to improve the lattice spacing in these regions to form crystallites. When vulcanization has reached the point where the network of primary valence cross-linkages noticeably reduce the plasticity, the internal stresses produced by stretching become effective in crystallite formation. This step demonstrates that vulcanization actually assists in the crystallization process. Once crystallization has started, anchorages are formed for adjacent portions of amorphous material, thus discouraging plastic flow and creating new points of stress for further crystallization. It is conceivable that, in the early states of vulcanization, such secondary bonds are more effective than the cross-linkages of the network. As vulcanization advances, there exists simultaneously the forces of crystallization and of increasing numbers of cross-linkages until an equilibrium between these two is reached and the optimum condition for crystallization is attained as shown by the maximum crystallinity appearing in the curve of Fig. 8. With additional cure, the complexity of the network increases and interferes more and more with the molecular mobility, thus reducing the possibility of forming crystallites. This is represented by that portion of the curve appearing to the right of the maximum.

TABLE II.

Compound	Cure		Stress at 500% Elongation kg/cm²	Tensile kg/cm²	Ultimate Elongation
	Min.	Temp. F°			
A	30	260	18	126	815%
B	10	260	70	244	675
C	20	260	28	166	770
D	15	285	29	160	765

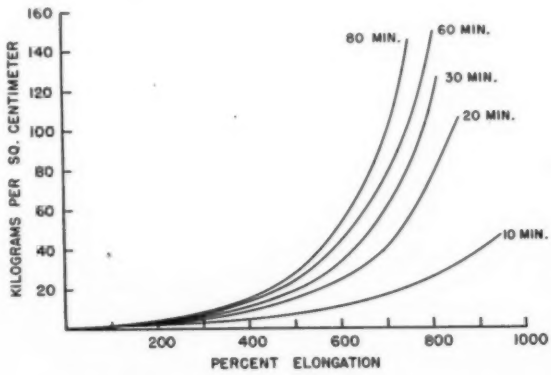

FIG. 9. Stress-strain curves for compound *A*.

The tensile strength of vulcanized rubber depends upon the extent of the vulcanization, and in considering a range of curing times, a peak or maximum tensile strength is reached as shown in Fig. 9. The cure producing a vulcanizate having the most desirable properties for a given purpose is considered as the "best cure." For this particular compound, (*A*), for general purposes, the "best cure," on the basis of practical experience, is judged to be the curing time that produces a vulcanizate whose tensile strength is about 10 percent less than the peak. On this basis, the 30-minute cure may be classified as the best cure. It is interesting to note that for this compound the most favorable condition for crystallite formation coincides approximately with the time for best cure.

The relationship between the crystallinity and the elongation, as it is effected by the curing time for vulcanizates *B* and *C*, is shown in Figs. 10 and 11, respectively. The crystallization decreases with the increasing curing times for these compounds. Obviously, the lowest cures for these compounds, according to Fig. 8, have either just reached the condition for maximum crystallinity or have already exceeded it.

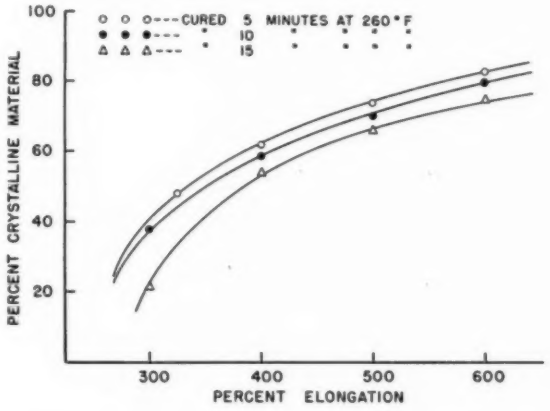

FIG. 10. Proportion of crystalline rubber in compound *B*.

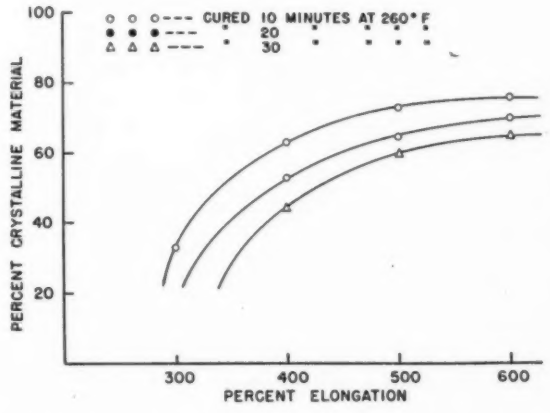

FIG. 11. Proportion of crystalline rubber in compound *C*.

TABLE III.

COMPOUND	PARTS BY WEIGHT							
	E	*F*	*G*	*H*	*J*	*K*	*L*	*M*
Rubber	100	100	100	100	100	100	100	100
Sulfur	3	3	3	3	—	3	3	3
Zinc oxide	5	5	5	5	—	5	5	—
P.P.D.	2	—	—	—	—	—	—	—
Captax	—	0.25	—	0.5	—	—	—	—
D.P.G.	—	0.25	0.5	—	—	—	—	—
Dinitrobenzene	—	—	—	—	10	—	—	—
Calcium oxide	—	—	—	—	—	—	10	—
Lead oxide	—	—	—	—	10	—	—	—

TABLE IV.

COMPOUND	CURE		STRESS AT 500% ELONGATION KG/CM²	TENSILE KG/CM²	ULTIMATE ELONGATION
	MIN.	TEMP. F°			
E	5	240	50	230	720%
F	20	260	33	220	790
G	40	285	28	148	760
H	40	260	18	136	830
J	20	285	18	54	740
K	180	285	7	46	935
L	80	285	20	97	825
M	240	285	6	31	1050

Different accelerators should have considerable effect on the crystallization in stretched vulcanized samples into which they have been incorporated on account of the various degrees of complexity and the type of network induced by their presence. The effectiveness of various accelerators on crystallite formation for a series of typical gum stocks at so-called "best cure" over a range of elongations is shown in Fig. 12. The composition of these stocks is shown in Table III.

Physical test data for these vulcanizates are tabulated in Table IV. The relative amount of crystalline material can be readily observed from these curves. At 500 percent elongation, for example, the P.P.D. vulcanizate *E* possesses the largest amount of crystallinity for the samples investigated. This is followed in order by compounds containing a Captax-D.P.G. mixture, *F*;

D.P.G., *G*; Captax, *H*; dinitrobenzene, *J*; ZnO, *K*; CaO, *L*; and straight sulfur, *M*. This sequence may be altered to some extent by variation in compounding or curing of stocks utilizing these same accelerators.

From the general appearance of Fig. 12, the curves fall into two groups, one with higher amounts of crystallinity for stretched samples

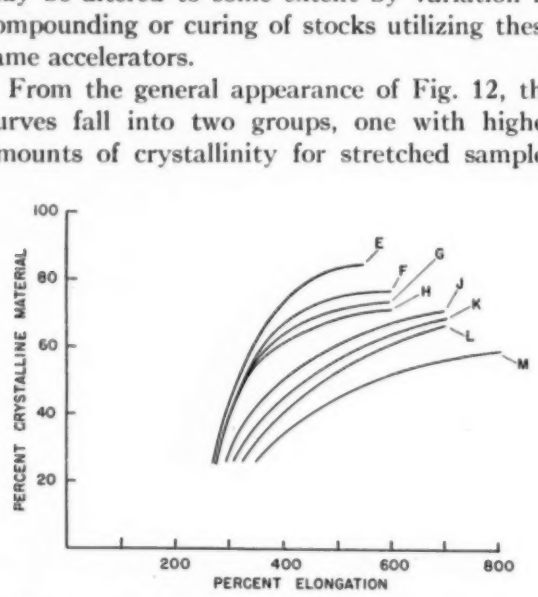

FIG. 12. Crystallinity of compounds with different accelerators

containing organic accelerators, and the lower group which includes the inorganic accelerators. Here the crystallinity approaches that in compounds cured with straight sulfur.

The influence of temperature on the formation of crystallites in stretched vulcanized rubber is shown in Fig. 13. At the same elongation, the number of crystallites is reduced as the temperature increases. This linear relationship may have some connection with the stress-temperature relation shown by Ornstein, Eymers, and Wouda.[21] The crystallinity before and after heating 15 minutes at 90°C, compared with the amount existing at 90°C, is shown in Fig. 14. As in the case of raw rubber, these patterns were obtained by re-exposing the same sample without retraction. The reduction in the number of crystallites at the higher temperature may be explained on the same basis as was discussed in the case of raw rubber. Since there was no measurable amount of set, it may be safely assumed that the network introduced by vulcanization has minimized plastic flow; thus no additional decrease in crystallinity would be expected from this source. This probably accounts for the re-establishment of the original amount of crystallinity at room temperature after the heat treatment. The effect of this heating on the cure was negligible. The crystallinity in evaporated latex sheets under the same conditions is also shown in this figure. The original amount of crystallinity at room temperature is practically the same for these raw and vulcanized rubber samples. The greater effect of temperature on the crystallinity for the raw rubber is clearly shown. At the higher elongations, where the crystallinity retards plastic flow in raw rubber, the difference in crystallinity occurring at 90°C and at room temperature after heating are about the same as that for vulcanized rubber. This is an indication of the way in which the structure of the raw rubber persists in the vulcanizate. Roughly, the plastic flow appears to be responsible for about one-half the decrease caused by heating in the crystallinity of stretched raw rubber.

CRYSTALLINITY AND CREEP PHENOMENA

The fundamental differences which may exist in the internal structure of stretched rubber, as previously disclosed, may find a direct correlation in some cases with physical behavior of the compounds. That this should be especially demonstrable in the case of creep phenomena can be

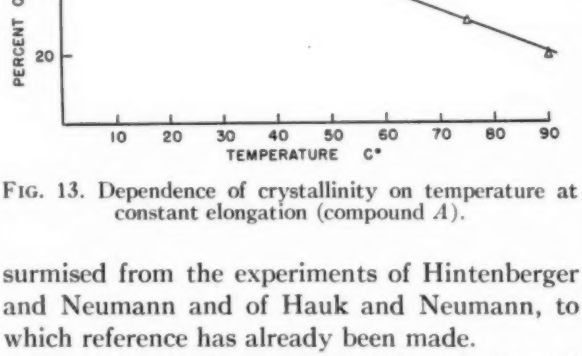

FIG. 13. Dependence of crystallinity on temperature at constant elongation (compound *A*).

surmised from the experiments of Hintenberger and Neumann and of Hauk and Neumann, to which reference has already been made.

When a strip of vulcanized rubber is subjected to a constant load over a considerable period of

time, an increase in length over the initial elongation occurs. This phenomenon is often referred to as "creep." Such changes in length are attributed to a gradual establishment of equilibrium between the liquid and crystalline phases in the rubber, a process into which x-ray diffraction studies should give some insight. Therefore, a more detailed investigation regarding the relation between the crystallinity and creep in rubber was carried out. It was of particular interest to follow the changes in structure occurring when a stretched sample was allowed to creep through the elongation at which crystallization ordinarily appears.

Samples were prepared by cutting uniform strips, 2 mm by 4 mm from similarly compounded vulcanizates, one a gum stock and the other with 48 parts of gas black. The composition of these stocks is shown in Table V.

TABLE V.

COMPOUND	PARTS BY WEIGHT *N*	*P*
Smoked sheet	100	100
Zinc oxide	3	3
Sulfur	3	3
Stearic acid	4	4
Captax	1	1
Agerite (phenyl-napthylamine)	1	1
Pine tar	3.75	3.75
Gas black	——	48

The physical properties for these vulcanizates are shown in Table VI. These were hung in a

TABLE VI.

COMPOUND	CURE MIN.	CURE TEMP. F°	STRESS AT 500% ELONGATION KG/CM²	TENSILE KG/CM²	ULTIMATE ELONGATION
N	70	260	46	188	670
P	70	260	208	288	610

cabinet, maintained at a constant temperature of 35°C, and stretched under constant loads by means of weights. For the compound with no black, a series of weights was used giving the following initial elongations: 140 percent, 185 percent, 210 percent, 235 percent, 280 percent, 370 percent, and 510 percent. Since crystallization ordinarily occurs at about 275 percent for this vulcanizate, the above range of elongations

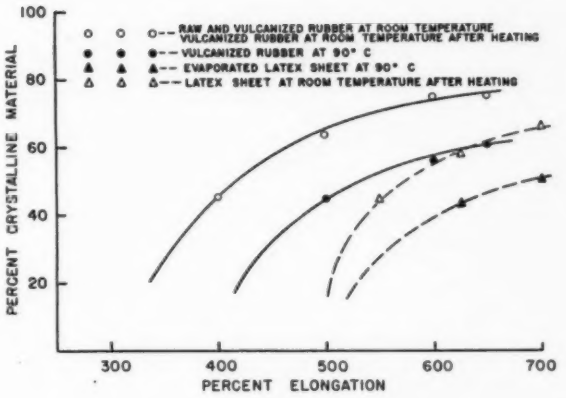

FIG. 14. Effect of temperature on crystallization.

covers the region above and below the point at which crystallites appear. Thus, the behavior in regard to crystallinity may be investigated as the rubber is permitted to stretch through the transition region in the neighborhood of 275 percent elongation.

For vulcanizates into which 48 parts of gas black is incorporated, the loads applied produced the following initial elongations: 60 percent, 75 percent, 110 percent, 135 percent, 170 percent, 180 percent, and 215 percent. For compounds with this quantity of gas black, about 150 percent elongation is sufficient to make crystallization evident.[22] This range of elongations lends itself to the same studies as the ones used for the compounds with no carbon black loading.

All of these samples were allowed to stand under constant load for about $3\frac{1}{2}$ months, during which interval measurements were made to follow the progress of the creep. The percent creep was determined by the ratio of the increase in elongation to the initial elongation. When the percent creep was plotted as a function of the time, typical creep curves were obtained as shown in Figs. 15 and 16. For the low stress of 97 g/sq. mm, in the case of the gum stock *N*, Fig. 15, the initial creep is low and the rate of creep is most rapid. For convenience, the stress is expressed here in terms of the cross-sectional area before stretching. As the stress is increased, the initial creep increases, with a corresponding decrease in the rate of creep thereafter. However, as Hauk and Neumann observed, a maximum is reached, and as greater stresses are applied, a smaller initial creep occurs, followed by a low

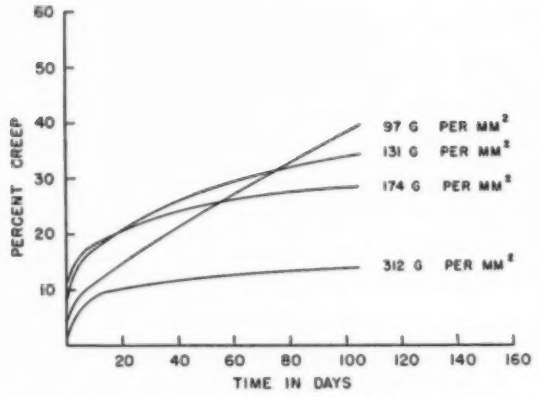

FIG. 15. Creep curves for vulcanized gum stock (N).

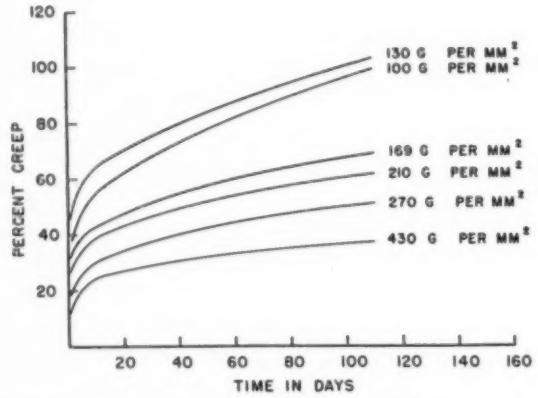

FIG. 16. Creep curves for vulcanized carbon black stock (P).

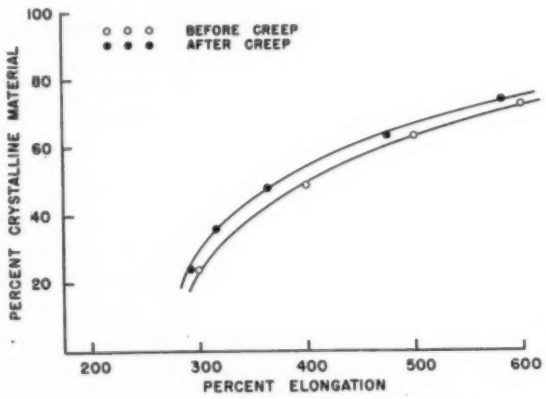

FIG. 17. Crystallization in gum stock (N) before and after creep.

rate of creep. The creep-time relation for the gas black stock P behaves in a similar manner, except that a greater amount of creep occurs than for the gum stocks, as shown in Fig. 16.

At the end of the $3\frac{1}{2}$-month period, the creep samples were clamped to aluminum strips while still under stress and x-ray diffraction patterns were recorded. The crystallinity as a function of the final elongation after creep is plotted in Figs. 17 and 18. The control curve in each case was obtained from x-ray diffraction data obtained immediately after stretching. For both the gum and carbon black stocks, the crystallinity is greater for the creep samples. The most obvious explanation for this is that as equilibrium between the liquid and crystalline phases is becoming slowly established, an opportunity is offered for additional crystallites to form over the number created immediately upon stretching. This has been verified to some extent by a stretched vulcanized rubber sample which was permitted to stand for two weeks at constant elongation. At the end of this time a substantial increase over the crystallinity present at the end of one day was noted, confirming observations of Thiessen and Wittstadt.[11]

Other interesting relations between the crystallinity and creep may be shown. One of these may be observed when these two quantities for the gum and carbon black stocks are plotted simultaneously as a function of the elongation, as shown in Figs. 19 and 20. In both instances, crystallization becomes evident as the creep reaches its maximum value. As was pointed out earlier, this maximum was explained by Hauk and Neumann as the combined effect of plastic flow and crystallization. The simultaneous relationship shown here is conclusive evidence of the effect of crystallization on the behavior of vulcanized rubber stretched under constant load. This

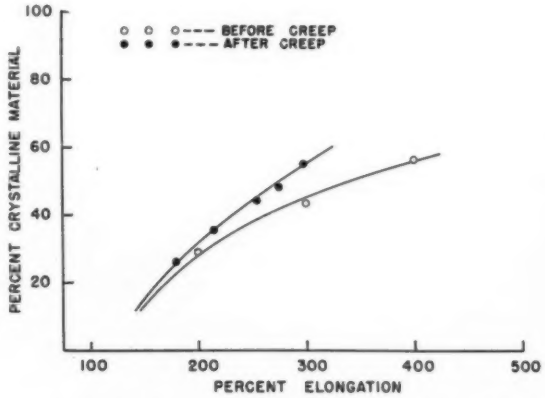

FIG. 18. Crystallization in carbon black stock (P) before and after creep.

effect is brought out in another way in Fig. 21, where the relation between creep and crystallinity is shown. The decrease in creep for the carbon black stock is approximately linear and coincides with the curve for the gum stock at the higher percentages of crystallinity. If it is assumed that crystallization has reached its maximum extent when no further creep occurs, then by extrapolation the proportion of crystalline material is shown to be about 85 percent of the total rubber. This is in substantial agreement with the amount previously determined for highly stretched rubber.

The larger creep for the carbon black stock as compared to the gum stock for low percentages of crystalline material, may find an explanation in the relatively poor alignment of the crystallites which exists in the carbon black stock.[22] For this reason, at least, the same degree of crystallinity in the two stocks does not imply the existence of identical internal structures.

Crystallinity and the Physical Properties of Rubber

In the discussion of creep phenomena, it was shown that the crystallization contributes an important, if not a major, part in the ability of rubber to withstand the high stresses generally associated with it. Since the physical properties of rubber may be controlled by the type of accelerator used, and the crystallinity has been shown to vary for different accelerators, some relationship between the crystallinity and the physical characteristics should be available.

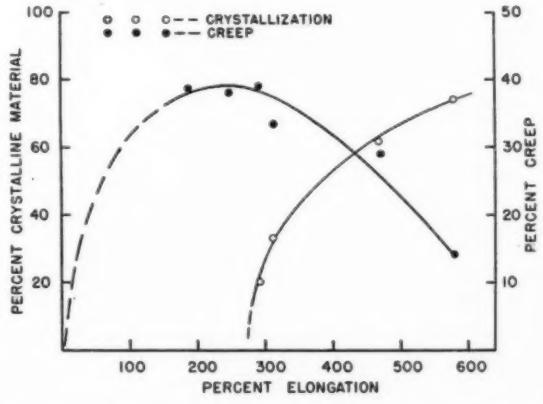

Fig. 19. Crystallization and creep as functions of the elongation (compound *N*).

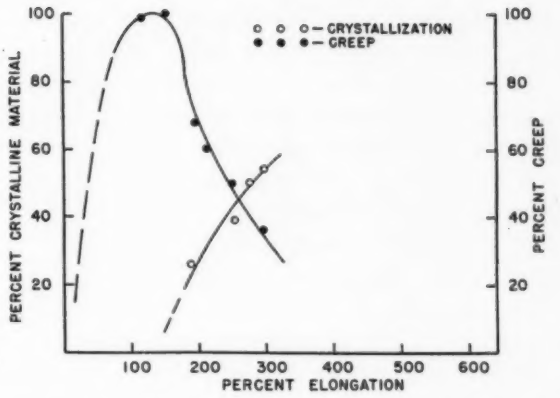

Fig. 20. Crystallization and creep as functions of the elongation (compound *P*).

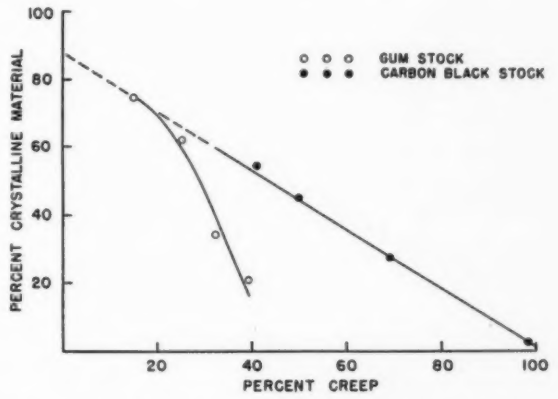

Fig. 21. Relation between creep and crystallization.

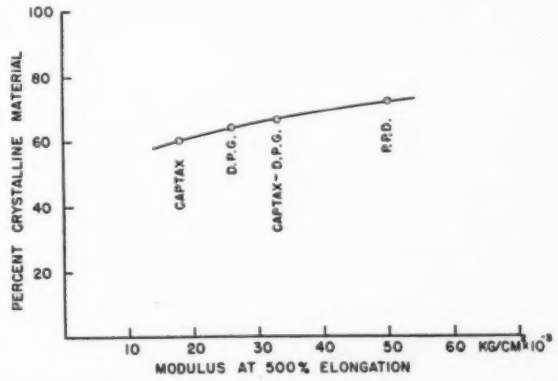

Fig. 22. Modulus *vs.* crystallinity for different gum stocks.

In rubber testing, a quantity widely used as a measure of the physical properties is the stress required to produce a given elongation. This is spoken of as a modulus. The crystallinity is plotted as a function of the modulus at 500 percent elongation for gum stocks cured with

different accelerators in Fig. 22. That crystallinity plays an important role in the strength of the rubber when it is stretched is verified, since the vulcanizate with the highest modulus also displays the greatest amount of crystallization. The data were obtained from patterns recorded for the "best cures."

When the crystallinity is compared with the modulus at 500 percent elongation for a technical range of cures of the same compound, as shown in Fig. 23, the modulus increases with cure and the crystallinity decreases. At first glance, these results would seem to be inconsistent with those obtained in connection with Fig. 22. However, they are comprehensible if considered in the light of the discussion pertaining to the mechanism of crystallization appearing elsewhere in this work. In the first place, the amount of crystalline material appearing in Fig. 22 was obtained from the "best cures" which should be somewhere near the curing time most favorable for crystallite formation. On the other hand, the crystallinity decreases with additional vulcanization due to molecular immobilization and the modulus indicates that the primary valence cross-linkages are becoming very effective in increasing the strength of the rubber. When this occurs, it generally reduces the extensibility of the rubber.

The crystallites in rubber give evidence for

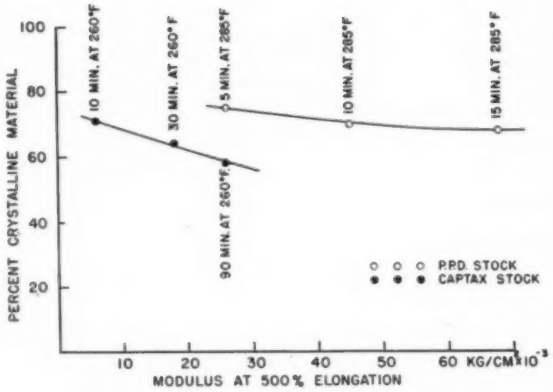

FIG. 23. Modulus *vs.* crystallinity for different cures.

the existence of a certain proportion of the hydrocarbon in a state which has a definite chemical and physical structure. The amorphous constituent, on the other hand, is more indefinite. Its exact constitution is probably never identical in different cases and eludes this x-ray analysis. Nevertheless, measurements of the proportions of these two fundamental components in stretched rubber can, from the foregoing, be judged to give many significant results.

The author wishes to express his indebtedness to Dr. S. D. Gehman for his helpful suggestions. Mr. M. J. DeFrance and members of the Research Compounding Division kindly furnished the vulcanized compounds used and the standard test data.

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Infra-Red Spectra of Rubber and High Polymers

By W. C. Sears

Physical Research Laboratory, B. F. Goodrich Company, Akron, Ohio

The transmission spectra of thin films of the following materials have been measured between 2.2μ and 14.8μ: crude rubber, soft and hard vulcanized rubber, thermoprene, polyvinylchloride, Neoprene and Pliofilm. The spectrum of rubber resembles that of the long chain paraffins more closely than do those of the polymers, polyvinylchloride, Neoprene and Pliofilm, all of which contain chlorine and have distinctive spectra. Vulcanization of rubber with 2.3 percent sulfur gives rise to no new bands in the region 2.2μ to 12.5μ characteristic of molecular cross bonding. Some of the bands in these materials are identified with valence vibrations.

Introduction

THE rubber industry is interested in all methods for studying the structure of highly polymerized substances. Infra-red spectroscopy has been recognized by recent workers[1,2] as a possible means for determining the valence forces in long chain molecules. Accordingly, the infra-red spectra of rubber and related compounds have been measured by several workers. An investigation of rubber, gutta percha, indene, polyindene, styrene, polystyrene, polyvinylacetate and polyvinylchloracetate has been carried out by Stair and Coblentz.[3] Later Williams[2] measured natural and vulcanized rubber, rubber hydrochloride, isoprene, styrene and polymerized butadiene in the region between 2.5μ and 9μ, but his spectra of rubber did not agree with that of Stair and Coblentz. Williams and Taschek[4] reported that the bands in rubber become broader with increasing stretch. Recently a rough survey of the infra-red transmission of rubber, Pliofilm, Vinylite XYSG, Shawinigan V-15, polystyrene, methyl methacrylate polymer and Cellophane has been made by Wells.[5] The Raman data of rubber obtained by Gehman and Osterhof[6] are in fair agreement with the infra-red results of Stair and Coblentz.

In the absence of a complete theory of the vibrations of chain molecules the interpretations of these spectra have been empirical. Thus a correlation of infra-red and Raman lines in molecules containing the same valence group (e.g., C−H, C=C, and C=O) has led to the association of a vibration frequency with each valence linkage. Hibben[7] lists the characteristic frequency and force constant for several types of linkage. Unfortunately considerable variation in some of these valence frequencies is observed. For example, valence vibrations involving the −C−C− linkage lie between 800 and 1100 cm^{-1}. In spite of frequent ambiguity in the designation of bands on this basis, the method has been useful in studying chemical structure and the mechanism of polymerization. Hibben's[8] Raman investigation of methyl methacrylate before and after polymerization indicates, by the disappearance of the C=C line, that polymerization is brought about by this group.

The regions of selective absorption in the infra-red correspond roughly to the frequencies of vibration and rotation of the atoms in a molecule. These frequencies usually are calculated by assuming a molecular model in which the atoms are acted upon by central or valence forces and by treating the model as a dynamical system having various normal modes of vibration. A normal vibration in polyatomic molecules does not necessarily take place along interatomic lines, but generally along intermediate axes. Therefore, it is not strictly proper to assign frequencies of polyatomic molecules to particular valence bonds. According to Wall[9] the frequency 990 cm^{-1} of ethane involves angle bending in the CH_3 group to a greater extent than displacement of the carbon atoms, even though this frequency is usually assigned to vibrations along the carbon-carbon bond.

Recently Whitcomb, Nielsen and Thomas[10] have formulated the most complete theory of the normal modes of vibration of an infinitely long chain composed of CH_2 groups. They assume a central force model wherein all carbon atoms lie in a plane (but not a straight line) with the hydrogen atoms situated symmetrically along the chain. Three of their normal modes of vibration are shown in Fig. 1, in which the frequencies stated are for $C_{11}H_{24}$. The vibration $\nu_2(o\pi)$ is interesting because its frequency 1463 cm^{-1} in the hydrocarbons usually has been assigned empirically to the deformation vibration $\nu_4(\pi\sigma)$ of the CH_2 group. In $\nu_4(o\sigma)$ there is a combination deformation and carbon-carbon valence vibration. Other normal modes of the hydrocarbons involve twisting and rocking motions of the CH_2 groups, as well as C−H vibrations. In their application of the theory to $C_{11}H_{24}$ the force constants between the hth CH_2 group and the $(h+2)$ and $(h-2)$ CH_2 groups are assumed negligible. In spite of this simplification there is good agreement between the observed and calculated frequencies in $C_{11}H_{24}$.

Considering the useful physical and chemical properties possessed by many long chain polymers, information concerning their structure is of vital importance to the organic chemist, through whose syntheses new products are made possible. Accordingly, it was thought worth while to investigate the infra-red spectra of crude rubber, soft and hard vulcanized rubber, thermoprene

TABLE I. *Compounding data of infra-red films.*

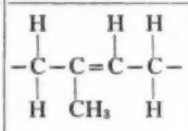
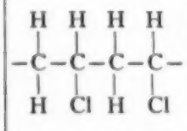
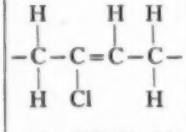
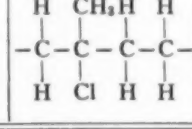
NAME	CHEMICAL FORMULA	COMPOSITION	SOLVENT	FILM		CURE
				METHOD	THICKNESS (CM)	
Crude rubber		pale crepe	gasoline	dip	0.0037	none
Hard vulcanized rubber		smoked sheet rubber 65.05% sulfur 20.75 accelerators and softeners 14.20	none	press	.0066	130 minutes @ 310°F
Soft vulcanized rubber		smoked sheet rubber 94.9% sulfur 2.3 stearic acid 0.9 zinc oxide 0.9 tetramethyl thiuram disulfide 1.0	gasoline	dip	.0061	30 minutes @ 206°F in steam
Rubber: S_2Cl_2 cured hard		35% latex		dip	.0045	48 hr. in S_2Cl_2
Thermoprene		cyclorubber	benzene	dip	.0053	none
Polyvinyl-chloride			methyl ethyl ketone	dip	.0053	none
Neoprene		Neoprene type E	benzene	dip	.0061	none
Pliofilm		commercial sample			.0040	none

TABLE II. *Comparison of the calculated frequencies of an infinitely long chain paraffin with those observed in crude rubber.*

Long Chain Paraffin: Calculated				Crude Rubber: Observed				
							Probable Origin	
Wave-length μ	Frequency cm^{-1}	$C_{11}H_{24}$ Relative Intensity I	Designation	Wave-length μ	Frequency cm^{-1}	Relative Intensity I	Designation	Frequency cm^{-1}
2.28	4389	6	$3\nu_2(o\pi)$					
3.54	2926		$2\nu_2(o\pi)$	3.45	2899	9	$2\nu_2(o\pi)$	2920
3.60	2778	10	$\nu_3(\pi\sigma)$				$\nu_3(\pi\sigma)$	2778
3.63	2752		$\nu_3(o\sigma)$				$\nu_3(o\sigma)$	
4.31	2320	6	$\nu_7(\pi\sigma)$					
4.40	2273	2	$\nu_7(o\sigma)$					
5.51	1814	5	$2\nu_4(o\sigma)$	5.95	1681	3	$2\nu_4(o\sigma)$	1692
6.84	1463	9	$\nu_2(o\pi)$	6.85	1460	9	$\nu_2(o\pi)$	1463
7.28	1374	8	$2\nu_6(\pi\sigma)+\nu_6(o\sigma)$	7.28	1374	7	$2\nu_6(\pi\sigma)+\nu_6(o\sigma)$	1460
7.39	1354	5	$\nu_9(o\pi)$	7.61	1314	5	$\nu_9(o\pi)$	1308
8.28	1208	4	$2\nu_6(o\sigma)$	8.10	1234	5	$2\nu_6(o\sigma)$	1200
				8.82	1134	6	—	
9.04	1106	5	$\nu_4(\pi\sigma)$	9.17	1091	7	$\nu_4(\pi\sigma)$	1106
9.63	1038	5	$\nu_5(o\sigma)$	9.65	1036	6	$\nu_5(o\sigma)$	1038
10.11	989	4	$\nu_6(\pi\sigma)+\nu_6(o\sigma)$	10.70	935	3	—	
				11.15	897	3	—	
11.03	907	8	$\nu_4(o\sigma)$	11.82	846	10	$\nu_4(o\sigma)$	907
13.00	770	4	$2\nu_6(\pi\sigma)$	13.25	755	5	$2\nu_6(\pi\sigma)$	770
16.56	604	6	$\nu_6(o\sigma)$	16.66*	600*	6	$\nu_6(o\sigma)$	604
25.97	385	4	$\nu_6(\pi o)$	23.2*	430*	4	$\nu_6(\pi\sigma)$	385

* A. J. Wells, J. App. Phys. 11, 137 (1940).

(cyclorubber), polyvinylchloride, Neoprene (polychloroprene) and Pliofilm (rubber hydrochloride). The measurements were made at the Mendenhall Laboratory of Physics, Ohio State University.

Experimental

Films of the various materials studied were prepared by dissolving them first in a suitable solvent. A wire ring was dipped into this solution, forming a film of suspended liquid. The solvent was allowed to evaporate, leaving a very thin film of solid within the ring. Films of crude rubber, thermoprene, polyvinylchloride and Neoprene were prepared in this manner, using the solvents indicated in Table I. Rubber films also were made by the dip method from latex. The hard rubber stock was calendered on tin and cured in a mold. The thickness of the various films as measured with an ordinary micrometer, ranged from 0.0037 to 0.0066 cm.

The infra-red transmission of these films was measured in the region between 2.2μ and 14.8μ on a Wadsworth-Littrow NaCl prism spectrometer of the type described by Strong and Randall.[11] Radiation from the optical part of the spectrometer was focused on a vacuum thermocouple, which was connected in series with a Leeds and Northrup galvanometer of sensitivity 0.0045μv/mm for the scale distance used. The ratio of the galvanometer deflection observed when the specimen was placed in front of the

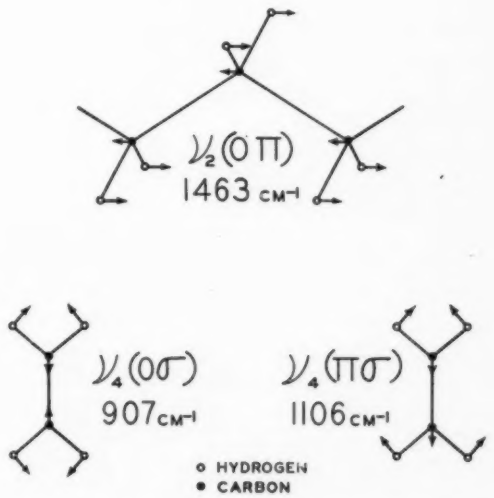


FIG. 1. Three of the normal vibrations of a long chain paraffin. In $\nu_2(o\pi)$ a portion of the molecule is viewed nearly perpendicular to the plane containing the carbon atoms; in $\nu_4(o\sigma)$ and $\nu_4(\pi\sigma)$ the molecule is viewed along the axis of least moment of inertia.

TABLE III. *Observed frequencies and estimated relative intensities of high polymers.*

Hard Vulcanized Rubber			Soft Vulcanized Rubber			Rubber: S_2Cl_2 Cured Hard			Thermoprene			Polyvinylchloride			Neoprene			Pliofilm		
Wave-length μ	Frequency cm^{-1}	Intensity I	Wave-length μ	Frequency cm^{-1}	Intensity I	Wave-length μ	Frequency cm^{-1}	Intensity I	Wave-length μ	Frequency cm^{-1}	Intensity I	Wave-length μ	Frequency cm^{-1}	Intensity I	Wave-length μ	Frequency cm^{-1}	Intensity I	Wave-length μ	Frequency cm^{-1}	Intensity I
3.41	2933	10	3.39	2950	9	3.41	2933	9	3.38	2959	10	3.40	2941	5	3.44	2907	4	3.39	2950	8
6.08	1645	6	5.96	1678	5	5.98	1672	4	5.80	1724	4	5.75	1740	4	5.95	1681	6	5.93	1686	3
			6.45	1550	4															
6.84	1462	10	6.83	1464	9	6.86	1458	10	6.80	1471	10	6.85	1460	7	6.86	1458	8	6.82	1466	9
7.25	1379	8	7.23	1383	7	7.25	1379	8	7.23	1383	7							7.18	1393	7
7.60	1316	7	7.56	1323	5	7.60	1316	6				7.40	1351	7	7.60	1316	9	7.60	1316	6
8.08	1238	8	8.07	1239	5	8.00	1250	7				7.95	1258	9	8.10	1235	8	7.90	1265	5
									8.30	1205	9	8.35	1200	3						
9.00	1111	9	8.82	1134	6	8.68	1152	6				9.06	1104	8	8.95	1117	10	8.65	1156	10
			9.17	1091	7	9.18	1089	8							9.20	1087	6	9.80	1020	5
9.65	1036	7	9.63	1038	6	9.75	1026	3	9.65	1036	8	9.73	1028	8	9.80	1020	8	10.20	980	3
10.25	976	7	10.22	979	4	10.23	978	4				10.25	976	9						
			10.75	930	3				10.63	941	1									
11.20	893	3	11.15	897	4	11.00	909	6	11.22	891	7				11.00	909	3	11.30	885	6
11.82	846	4	11.82	846	10	11.81	847	7	12.00	834	6	11.55	866	6	11.95	837	10	11.80	848	6
12.50	800	2																12.30	813	7
13.20	758	5							13.25	755	3	14.05	712	7	12.75	784	7	13.25	755	8

spectrometer slit to the deflection observed when the specimen was out of the optical path gives the percentage transmission. Each film was adjusted in the path of the beam to give greatest transmission and least scattering.

The results are plotted in Figs. 2, 3 and 4 as percent transmission against wave-length and frequency. The curve for $C_{11}H_{24}$ is reproduced here from the work of Whitcomb, Nielsen and Thomas[10] for comparison with rubber. In Table II their calculated frequencies for an infinitely long chain paraffin are compared with those observed in crude rubber. The observed frequencies and relative intensities of the vibration bands in hard vulcanized rubber, soft vulcanized rubber, rubber cured hard in S_2Cl_2, thermoprene, polyvinylchloride, Neoprene and Pliofilm are given in Table III.

Discussion

A similarity is observed (Fig. 2 and Table II) between the spectra of crude rubber and $C_{11}H_{24}$, which appears to be more than accidental. The strong C−H valence vibrations, $\nu_3(\pi\sigma)$ and $\nu_3(o\sigma)$, in the region of 2900 cm^{-1} in $C_{11}H_{24}$ are also present in rubber, but the two weak C−H bands, $\nu_7(\pi\sigma)$ and $\nu_7(o\sigma)$, near 2300 cm^{-1} are absent in rubber. The band at 1814 cm^{-1} in $C_{11}H_{24}$, which is designated as the first harmonic of $\nu_4(o\sigma)$ at 907 cm^{-1}, appears to correspond to the 1681cm^{-1} band in crude rubber, a first harmonic of

FIG. 2. Infra-red spectra of $C_{11}H_{24}$, crude and hard vulcanized rubber.

the strong vibration at 846 cm^{-1}. Instead of the band at 1681 cm^{-1} observed in this work Williams[2] reported a band at 1725 cm^{-1}, which he designated as the first harmonic of an unobserved fundamental. Also, he observed a band at 1600 cm^{-1}, a $-C=C-$ vibration according to his assignment. Stair and Coblentz likewise obtained only the one band at 1681 cm^{-1} for rubber. The same spectra have been obtained in the present work for pale crepe rubber and evaporated latex.

If the band at 1681 cm^{-1} in crude rubber is due to $-C=C-$ bonds, its intensity should nearly vanish in hard vulcanized rubber, which is supposed to contain very few double bonds. On the contrary, this band is more intense in rubber vulcanized hard with sulfur and with S_2Cl_2 than in crude rubber. The bands at 979 and 1550 cm^{-1} in soft vulcanized rubber (Fig. 3), which were also present in the uncured compound, may be due to some curing ingredients. Otherwise, the frequencies and relative intensities in soft vulcanized rubber are the same as those in crude rubber.

The parallel vibration $\nu_2(o\pi)$ at 1463 cm^{-1} in $C_{11}H_{24}$ also is found in rubber before and after

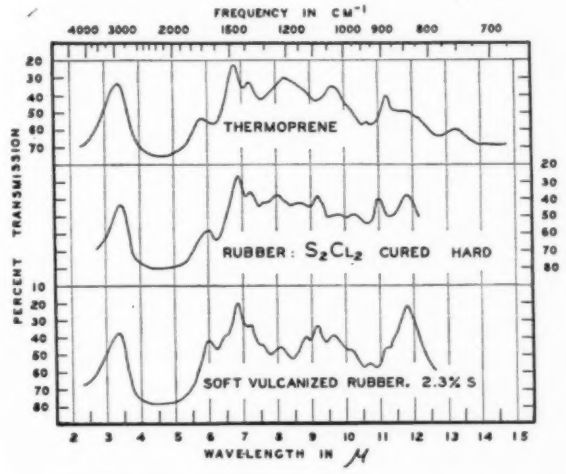


FIG. 3. Infra-red spectra of thermoprene (cyclorubber), rubber cured 48 hours in S_2Cl_2, and soft vulcanized rubber.

vulcanization, thermoprene, polyvinylchloride, Neoprene and Pliofilm at very nearly the same frequency. This vibration is one in which the carbon and hydrogen atoms move along the axis of least moment of inertia of the molecule in

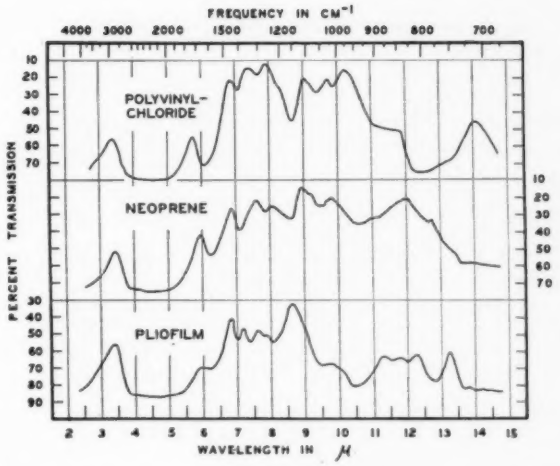


FIG. 4. Infra-red spectra of polyvinylchloride, Neoprene (polychloroprene) and Pliofilm (rubber hydrochloride).

opposite directions. The band at 1374 cm^{-1} in $C_{11}H_{24}$ is said to be a combination band, while $\nu_9(o\pi)$ at 1354 cm^{-1} involves a twisting motion of the CH_2 groups. Stair and Coblentz and the writer find a band at 1234 cm^{-1} in rubber, which Williams did not observe. The angle deformation vibration $\nu_4(\pi\sigma)$ at 1106 cm^{-1} in $C_{11}H_{24}$ also may be active in rubber, but its frequency is uncertain. Very likely the band at 846 cm^{-1} in rubber corresponds to the C–C vibration $\nu_4(o\sigma)$ at 907 cm^{-1} in $C_{11}H_{24}$.

Many bands in vulcanized hard rubber appear at the same frequencies as in crude rubber, but the region 950 cm^{-1} to 1700 cm^{-1} is greatly intensified by vulcanization. In general, new vibrations characteristic of vulcanization (sulfur and new $-C-C-$ bonds within or between rubber molecules) may be expected at frequencies below 1000 cm^{-1}. The $-C-S-$ linkage is reported[7] to have a characteristic frequency at 675 ± 25 cm^{-1}, but no band is observed here in vulcanized rubber. Absorption from $-S-S-$ linkages at about 500 cm^{-1}, as in the polysulfides, is beyond the range of the present work. The new band at 976 cm^{-1} in hard rubber may arise from $=C=S$ linkage vibrations, which are supposed to obtain at 1072 cm^{-1}.

The new band at 909 cm^{-1} in rubber cured in S_2Cl_2 (Fig. 3) cannot be identified with any of the frequencies of S_2Cl_2. The spectrum of thermoprene is similar to that of crude rubber, but it also has new bands at 891, 1036 and 1205 cm^{-1}, which

cannot be identified empirically as valence vibrations.

The spectra of the long chain polymers, polyvinylchloride, polychloroprene and rubber hydrochloride, might be expected to differ widely from those of the hydrocarbons because they all contain the heavy atom, chlorine. Many new, intense bands appear in polyvinylchloride and the commercial materials known as Neoprene and Pliofilm (Fig. 4) which readily distinguish each of these substances from rubber and the hydrocarbons. The C−H bands in the region 2900 cm^{-1} of polyvinylchloride and Neoprene are less intense than those in the saturated paraffins. The bands at 1740 cm^{-1} in polyvinylchloride, 1681 cm^{-1} in Neoprene and 1686 cm^{-1} in Pliofilm are believed to be partly harmonics of fundamentals in the region of 850 cm^{-1}. The vibration $\nu_2(o\pi)$ at 1460 cm^{-1} remains almost unchanged from its position in the hydrocarbons in all three of these substances. A C−Cl vibration, such as is observed in methylchloride at 732 cm^{-1}, may be present at 712 cm^{-1} in polyvinylchloride, 784 cm^{-1} in Neoprene and 755 cm^{-1} in Pliofilm.

All the bands of polyvinylchloride in the present work correspond directly with those obtained by Stair and Coblentz[3] for polyvinylacetate in the region between 2.2μ and 11μ. This agreement is not surprising in view of their known similarity of chain structure. Moreover, it indicates that the perturbation of the chain vibrations produced by the acetate side group in polyvinylacetate and by the chlorine in polyvinylchloride is roughly the same. On the other hand, the infra-red spectra of polystyrene (polyvinylbenzene) measured by Stair and Coblentz[3] shows that it has a different chain structure from polyvinylchloride and polyvinylacetate.

The assignments of the vibration bands of complicated molecules to particular valence bonds is not only uncertain, but also there remains a large number of bands unexplained. Calculation of the normal modes of vibration for each of these high polymers using the method of Whitcomb, Nielsen and Thomas might account for their observed spectra and give valuable information concerning their structure. The similarity between the spectra of rubber and $C_{11}H_{24}$ between 2.2μ and 14.8μ suggests that the bands for rubber in this region arise from interatomic vibrations of relatively short sections of the chain. The low frequency vibrations (below 700 cm^{-1}) of these high polymers, which are characteristic of interlocking and cross bonding, should be investigated in order to obtain information about the molecular arrangement.

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Some Applications of the Kinetic Theory to the Behavior of Long Chain Compounds

BY H. MARK

Brooklyn Polytechnic Institute, Brooklyn, New York

IF long chain molecules pass from the extended into the contracted state a certain amount of curling energy and curling entropy may be developed. In recent years several authors have discussed these energy and entropy changes in connection with the elastic properties of long chain high polymers.[1] In the following a few remarks will be made as to their importance on other properties of such systems.

1. The Melting Points of Long Chain Compounds

Thermodynamics show that the temperature of fusion of a crystallized substance is given by

$$T_f=\frac{\Delta H}{\Delta S}, \tag{1}$$

where ΔH represents all energy and ΔS all entropy changes which are involved during the transition from the solid into the liquid phase.

In long chain molecules ΔH can generally be expressed by

$$\Delta H=q_0+n\cdot q, \tag{2}$$

where q_0 accounts for the influence of the end groups, while q is the increment of the heat of crystallization per elementary unit of the chain; n being the number of links. According to Garner and King[2] the values of q are constant for a given homologous series and range between 610 cal. per methylene group (in the vertical forms of even hydrocarbons) and 1080 cal. per methylene group (in the tilted forms of even methylester of fatty acids). The values for q_0 are between -530 and -3900 cal. per end group; the negative sign has been discussed and explained by Garner and King. If n exceeds twenty, the influence of the end groups can be neglected without committing a too great mistake. Therefore for long chains we may put

$$\Delta H=n\cdot q.$$

This would mean that, if no entropy changes were involved, the melting point of long chain compounds should increase with the chain length and should be proportional to the molar cohesion q of the elementary unit. However this is only true in a limited range of n (according to Garner and King if n is about between 10 and 30) while for longer chains the melting points tend to a convergence temperature. Very careful experiments and calculations of Garner and King and recently of Hibbert and Huggins[3] have shown that this convergence temperature lies in the range between 380 and 410° K.[3]

Taking into account the statistical theory of long chain molecules, the following explanation may be suggested for this behavior.[4]

The entropy of fusion of long chain molecules will obviously have the form

$$\Delta S=s_0+s(n), \tag{3}$$

where s_0 represents the entropy gain caused by the fact that the center of gravity of the molecules is set in freedom and, instead of vibrating around a fixed equilibrium position in the solid state, carries out a Brownian movement in the liquid state (macro-Brownian movement of Kuhn). This entropy gain will be in first approximation independent of n. The term $s(n)$ on the other hand represents the entropy gain due to the fact that certain internal vibrations and rotations, which were frozen in in the crystal are occurring in the melt (micro-Brownian movement of Kuhn). The present elementary theory of the internal statistics of long chain molecules gives for $s(n)$ in the case of normal paraffins and under the assumption of free rotation about the single carbon-carbon bond

$$s(n)=1.04k\left[n-1.6\sqrt{n}+0.67-1.6\frac{1}{\sqrt{n}}+\frac{1}{n}\right] \text{ erg pro grade.} \tag{4}$$

For the temperature of fusion we have generally

$$T_f=\frac{q_0+nq}{s_0+s(n)}, \tag{5}$$

which gives for very long chains ($n\gg1$)

$$T_f=\frac{q}{1.04\cdot k}. \tag{6}$$

Taking the experimental values for q between 610 and 1080 cal. per mol CH_2 one gets for the temperature of convergence values in the range between 286° and 495° which is in not too bad agreement with the experimental facts (380°–410°).

The important influence of a possible entropy gain during fusion has been emphasized recently by Baker and Smyth[5] in a series of very interesting investigations. Apparently it also shows up in the behavior of long chain compounds.

If one wants to raise the melting point or softening range of a chain high polymer (e.g., polystyrene, polyisobutylene or ethylcellulose) one has obviously two possibilities:

(a) Increasing ΔH. This means to introduce groups with a higher molar cohesion into each (or at least nearly each) link of the chain. This influence accounts presumably for the increased thermostability in the series ethylcellulose-cellulose acetate-cellulose or acrylic methylester-methacrylic methylester-acrylonitril.

(b) Decreasing Δs. This means to reduce the entropy gain during melting and therefore making the liquid state less probable and hence less desirable from statistical point of view. This is presumably the reason why a very few cross linkages lift the softening zone of polymers quite considerably. Divinylbenzene in polystyrene; divinylether in polyvinyl acetate, vulcanization of rubber, etc.

In some cases (cellulose, polyesters, polyamides, polyacrylic acid, polyvinyl alcohol) substitution of groups with different molar cohesion is not too difficult and therefore mainly used for the above purpose; in other cases however (rubber, polyolefines, polyvinyl halides) it seems that the decrease of the curling entropy (crosslinking and stiffening) is the more prominent way to produce higher melting systems.

2. *The Swelling of Long Chain Compounds*

The tendency of a low molecular solvent (toluene, acetone etc.) to enter a high polymer compound (rubber, cellulose acetate, etc.) is determined by the change of the free energy of the system

$$\Delta F=\Delta H-T\cdot\Delta S. \tag{6}$$

In this expression ΔH stands for the action of the forces between solvent and gel, while ΔS measures the entropy change, which accompanies the swelling process. In order to get an insight into how these two influences combine and overlap each other, it is necessary to have both ΔH and ΔS measured independently. Not very much experimental material was available until the last few years.

Recently, however, K. H. Meyer[6] has started with several collaborators a systematic investigation of long chain compounds, which has greatly improved our knowledge in this field. He finds that always, if long chain high polymers are involved, the entropy gain which accompanies the entrance of one mole swelling agent into the dry polymer exceeds considerably the value of the classical mixing entropy per mole $-R\ln N_2$. This seems to be true regardless whether ΔH is positive, zero, or negative.

Meyer explains this behavior by a statistical consideration of the possible arrangements of a small molecule, which enters a long chain micellar system and shows that such an excess of entropy gain has to be expected.[7] It is only another expression of this idea, which has also been forwarded by Haller[8] and Kuhn[9] if we apply Eq. (4) on this case.

In the unswollen state each chain will along a certain length (20 to 1000A) be embodied into a lattice-like structure (micellae, crystallized areas, crystallites). Sometimes (cellulose, polyamides, silk) these crystallites are so large, that one gets fair x-ray patterns; sometimes (rubber, polyvinyl chloride, polyisobutylene) they are so small that one only observes an amorphous halo.[10] In these latter cases however crystallization can always be produced by stretching the sample and parallelizing the chains.

If a swelling agent enters such a chain polymer it will in any case increase the internal mobility

and fluidity of the system and hence mobilize a fraction of the curling entropy of the chains. It will therefore act similarly as a rise of temperature does and it may therefore be not too inappropriate to apply to this case the considerations developed in the foregoing paragraph.

If one wants to reduce swelling (which is often of importance) one can again (a) Increase the molar cohesion between chains or (b) Decrease the entropy gain during swelling.

It is quite significant that (in contrast to the melting properties) now case (a) cannot easily lead to a general success, because any kind of substituent with high molar cohesion will attract equally well the swelling agent (nitrocellulose swells as well as ethylcellulose if one chooses an appropriate swelling agent). Sometimes it seems that a reduction of the molar cohesion even decreases swelling (methylrubber, rubber, polybutadiene). But (b) leads in all cases to a distinct drop in the tendency to take up a solvent (cross linking, branching, copolymerization) even if the amount of cross linking is relatively small.

It seems to be impossible to give any kind of reasonable quantitative prediction of this influence, because ΔH plays a very much more complicated role than in the case of fusion. But it may be not superfluous at least to estimate the order of magnitude and to compare it with the observations.

K. H. Meyer and his collaborators[11] observed that the swelling entropy of 1 g rubber in 1 g toluene amounts to about $1.89 \cdot 10^{-3}$ cal. per gram rubber. The total contraction entropy of one gram rubber of a molecular weight of 50,000 (if all chains would pass from the completely extended state into the state of maximum entropy) is $3 \cdot 10^{-2}$ cal. per gram. This means that already about 6 percent of this total curling entropy is sufficient to explain the experimentally observed values of the anomalous swelling entropy.

3. *The Viscosity of Diluted Solutions of Soft Elongated Particles*

In a recent paper Mehl, Oncley, and Simha[12] have given a very interesting list concerning the asymmetry of protein molecules in diluted suspensions. They show that such substances as egg albumin, serum albumin, hemoglobin, etc., have presumably the average shape of an elongated ellipsoid of revolution. If one calculates the axis ratios $f = a/b$ from viscosity measurements and compares them with the corresponding values from diffusion experiments in the ultracentrifuge, one gets according to Mehl, Oncley, and Simha the values shown in Table I for the above-mentioned substances.

TABLE I.

SUBSTANCE	f FROM VISCOSITY	f FROM DIFFUSION
egg albumin	5.0	3.8
serum albumin	5.6	5.0
hemoglobin	4.6	3.7

Although these values correspond very well in the order of magnitude it seems that in general the axis ratio calculated from viscosity exceeds that computed from diffusion by about 10–20 percent. The particles behave as if they were more elongated in the viscometer than in the ultracentrifuge. It seems to be doubtful whether the above effect is real, because, as Mehl, Oncley, and Simha point out, the f values from viscosity are subject to certain assumptions concerning Brownian movement and solvation. But if it should prove to exist, then the following explanation may be suggested.[13]

In the viscometer each particle is subjected to a certain shearing force, which will try to elongate it and will therefore increase its axis ratio. No similar force is acting on the particle in the ultracentrifuge. The shearing force τ is given by

$$\tau = \eta \frac{dv}{dr}, \qquad (7)$$

η = viscosity of the solvent,

$\frac{dv}{dr}$ = velocity gradient of flow.

In a capillary viscometer one gets

$$\tau = \frac{1}{2} \cdot \frac{\Delta p}{l} \cdot r,$$

Δp = pressure difference which causes the flow,

l = length of capillary tube,

r = radius at which one wants to have τ.

The average shear is therefore

$$\tau = \frac{1}{4} \cdot \frac{\Delta p}{l} \cdot a,$$

a = radius of capillary tube.

If one assumes $l = 10$ cm, $a = 3 \cdot 10^{-2}$ cm, and $\Delta p = 10$ g (which are normal experimental conditions), one gets an average shear of 7.5 dynes. Assuming that the diameter of the suspended particles is around 30A, the particles will be subject to a force of about $2.3 \cdot 10^{-6}$ dyne. On the other hand the force to elongate a single normal hydrocarbon chain is given by

$$\sigma = \frac{3kT}{nl_0^2} \cdot \frac{1-\cos\alpha}{1+\cos\alpha} \cdot \Delta l. \qquad (9)$$

Taking $T = 300$, $n = 1000$ (molecular weight 14,000), $l_0 = 1.55$A and $\alpha = 110°$, one gets

$$\sigma = 0.82 \cdot \Delta l.$$

In order to obtain 20 percent increase of f one has to stretch the above particle by $\Delta l = 6 \cdot 10^{-8}$ cm and finds that the force which is necessary to produce such an elongation amounts to

$$\sigma \sim 5 \cdot 10^{-7} \text{ dyne.}$$

Comparing this with $2.3 \cdot 10^{-6}$ dyne we see that the shearing forces in a capillary viscometer under normal working conditions are strong enough to produce a sensible elongation of dispersed particles having chain structure, polymerization degrees around 1000 and sufficient internal mobility.

It would certainly be premature to carry out further calculations without having more detailed experimental data. The scope of this short note was only to show that the shearing forces in a viscometer are of the order of magnitude to produce stretching of suspended particles with rubber-like elasticity.

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Physical Characteristics of Synthetic Rubbers

BY J. N. STREET AND J. H. DILLON

Firestone Tire and Rubber Company, Akron, Ohio

A summary of the nature and special applications of the more important types of synthetic rubbers is given. Two series of rubber and synthetic rubber stocks, compounded on the basis of comparable pigmentation, were selected for study. In addition to the conventional physical properties (tensile strength and elongation at rupture, modulus, aging, etc.), a number of other mechanical properties such as dynamic rigidity, hysteresis loss, "blowout resistance," "running temperature," and tensile strength at elevated temperature were measured. Swelling tests in various solvents were also made. Results are plotted in the form of correlation charts in an effort to select proper methods of measurement. Some observations on comparative service tests in tires in the case of three synthetic rubbers indicate them to be satisfactory, on a quality basis, for use in time of emergency. The importance of care in selecting the proper physical tests and methods of analysis is emphasized in the light of the results given. It is concluded that rubber testing techniques and interpretation must be modified in certain instances in evaluating synthetic rubber stocks.

OVER forty years ago, efforts were made to create a synthetic rubber. While these early efforts were undoubtedly more of academic interest than practical in nature, they laid a groundwork for our present materials. They were directed toward the development of a true synthetic rubber, in an effort to duplicate rubber and thereby establish its structural make-up.

During the last war, activity in this line in Germany was shifted toward producing a usable material as a substitute for rubber for tires and other products. The blockade had become sufficiently effective to embarrass the German military machine because of the lack of the natural product. The German efforts, which resulted in the development of "methyl rubber," did not attain sufficient success to warrant continuation along the same line after the close of the war.

In this country, following the war, the subject of synthetic rubber was approached from the standpoint of producing a rubber-like material that would be of commercial value because of properties different from those of rubber. Instead of looking toward the development of a product which would replace rubber, the major objective was finding an elastic material which would satisfactorily withstand conditions under which our natural rubber failed in a comparatively short time.

While rubber, in the form in which nature produces it, has many useful qualities, it also has a few properties which limit its applicability in certain types of service. These are mainly the lack of resistance to oils and various chemicals and also susceptibility to the deteriorating effect of the usual atmospheric conditions. The latter is primarily an oxidation effect although it may be apparent in different forms, such as the cracking or crazing of surfaces exposed directly or indirectly to sunlight, or a loss of tensile strength on long exposure without light. The latter is considerably accelerated at higher temperatures, thus limiting usage under such conditions.

The du Pont Company has achieved considerable success in the effort to produce a material fulfilling the original premise as to the commercial requirements of such a synthetic with the product which has been called "Neoprene," and which has been on the American market for the last eight years. Its raw materials are, mainly, acetylene and hydrochloric acid.

In Germany, the subject of synthetic rubber again became active about eight or ten years after the last war. In all probability, the seeds of the present situation were being sown and efforts were directed mainly toward a substitute for rubber. These efforts culminated in a group of materials which were announced about six years

ago under the name of "Buna" rubber. The important members of this group are made from butadiene copolymerized with other materials. When acrylonitrile is used as the copolymer, the product is called "Buna N." This product is highly oil-resistant and, consequently, might be termed a specialty rubber, which can probably create a market in open competition with crude rubber and other synthetics. When styrene is the copolymer, the resulting product is called "Buna S." This product is not oil-resisting and its only apparent useful purpose is to replace natural rubber in time of shortage.

In addition to these types of synthetics, there has also been developed, both here and in Europe, a group of materials such as Thiokol, Koroseal, Vistanex, and others whose characteristics are more those of a flexible plastic, rather than those of rubber. These materials as a class, are, in general, too thermoplastic to meet the demands of a large proportion of our rubber products. They lack the resilience characteristics required of parts used under appreciable mechanical action. They are, however, useful products for service where flexibility is required, but a high degree of elasticity is not essential.

More recently, the growing seriousness in world affairs has caused a marked increase in interest in this country in rubber substitutes as well as synthetics for specialized usage. This has led to the development of Ameripol, Synthal and Chemigum, which have just recently been announced. No technical information as to their properties has as yet been released. The fact that they are made from butadiene, as are the Bunas, and by somewhat similar processes, leads to the assumption that they will have somewhat similar basic characteristics which seem to be associated with this group of polymers.

Similarly, butyl rubber has been announced as being still another type of product, differing from any thus far discussed. Here again the rubber industry awaits with interest the completion of this development to a point where physical characteristics and samples are available.

In view of the foregoing remarks, the synthetics selected for comparison with respect to physical properties are Neoprene, Buna N, Buna S, Thiokol, and one or two experimental materials which may be of interest from a purely physical standpoint.

In making this comparison, it must be remembered that there is no true synthetic rubber. The synthetics all differ from natural rubber in chemical constitution.[1] Hence, only because of physical similarities of rubber and the synthetics, are we justified in using the term "synthetic rubber." Since this is now common usage, it will be employed rather than the newly coined word "elastomer."

Compounding Formulas

In making a comparison of different polymers, the first problem is that of selecting the basis of formulation. The Buna type products, compounded with necessary curing ingredients but without reinforcing pigments, have low tensile strength—of the order of 1000 lb. per sq. in. Carbon black exerts a much more pronounced reinforcing action than in the case of rubber. However, zinc oxide does not show nearly as great a reinforcing effect as in the case of rubber. Consequently, some channel black must be used with the Buna types if the best characteristics are to be brought out. On the other hand, Neoprene shows high tensile strength in gum type formulas and does not appear to give the tensile strength improvement expected from the compounding of a reinforcing pigment, when carbon black is included.

The logical approach would be to compound each material so as to give the most serviceable product. Requirements from product to product vary so much, however, that such a basis would lead to specific rather than general conclusions, besides involving the presentation of too much data to be adequately handled. Again, many automotive parts are specified in terms of durometer hardness. To meet such a specification with different polymers would require marked differences in compounding from polymer to polymer. In view of this situation, we propose to review briefly the physical properties of tread type and of a moderately hard and of a moderately soft motor support type formulation, for each

[1] L. A. Wood gives an excellent summary of the chemical structures of the synthetics and a very complete bibliography of work in this field in Circular of the National Bureau of Standards C427 *Synthetic Rubbers: A Review of their Compositions, Properties, and Uses* (June, 1940).

material. This permits the setting up of the compounds on a basis of comparable pigmentation. On this basis, swelling tests can be interpreted in terms of the characteristics of the base polymer. Compression set tests probably can be extrapolated to stocks of comparable hardness. In reviewing a group of properties on this basis, it must be taken into consideration that the best properties obtainable with any one of the polymers, including rubber, are not brought out. The selection of curing ingredients, softeners, etc., must be such as to strike a mean over such properties as permanent set, efficiency, oil resistance, etc. All stocks tested were cured to a flat optimum tensile state.

The formulas used are shown in Table I. The volume ratio of pigment to polymer has been maintained constant in the series of motor support stocks. In the case of tread formulas this is not true. Slightly higher ratios of carbon black to polymer have been used in Buna type compounds as laboratory tests indicated this to be desirable. It is quite possible that more extensive service tests now in progress may show that this is not the case.

TABLE I.

	Base Formulas				
	Rubber	Neoprene	Buna N Type	Buna S Type	Thiokol
Polymer	100	100	100	100	100
Sulfur	3		2	2	
Zinc oxide	5	5	5	5	8
Magnesia		4			
Stearic acid	3	0.5	2	2	0.5
Oils	2	4	3	3	
Latac		0.5			
Antioxidant	1	1			
Captax	1		1		
Altax					0.15
Santocure				1	
Moderately hard motor support					
Carbon black	30	22.5	29	29	
P-33	45	33.5	43.5	43.5	
Moderately soft motor support					
Carbon black	15	11.2	14.5	14.5	
P-33	20	15	19.4	19.4	
Tread stocks					
Carbon black	50	37	50	55	

TABLE II.

Tensile strength—lb./in.²

	Tread Stock	Hard Motor Support	Soft Motor Support
Rubber	4400	3500	3900
Neoprene	3800	2675	3200
Buna N type	3600	3050	2200
Buna S type	3300	2200	2100

400% Modulus—elongation at rupture

	lb./in.²	%	lb./in.²	%	lb./in.²	%
Rubber	2100	600	2175	600	1400	650
Neoprene	2700	550	1675	500	1250	740
Buna N type	1500	580	3050	400	2100	410
Buna S type	1500	600	2000	430	1950	430

Curing and softening ingredients in the Neoprene have been selected as a compromise between efficiency and permanent set. The Buna N type formula with this low amount of softener is undoubtedly not commercial.

Tensile Properties

The tensile strength at rupture in tread and motor support compounds is given in Table II. It is noted that all the synthetics have lower tensile strength than rubber in equivalently compounded stocks. These values are representative of those producible in factory practice. Under optimum milling conditions in the laboratory, higher tensile stocks can be attained. For example, with due precautions, Buna N type products with tensile strengths of nearly 5000 lb./in.² can be obtained in laboratory mixed stocks. Similarly, Buna S stocks with tensile strengths of 4000 to 4200 lb./in.² can be prepared in the laboratory. It should be noted, comparing only the hard *vs.* the soft motor support stocks, that the addition of black has increased the tensile of the Buna stocks, whereas the opposite is true for the rubber and Neoprene stocks.

Aging and Rupture

Conventional rupture and aging data for the two groups of motor support stocks are summarized in the form of a chart in Fig. 1. The stocks given at the left refer respectively to the horizontal lines upon which the properties listed at the top are plotted with quantities increasing

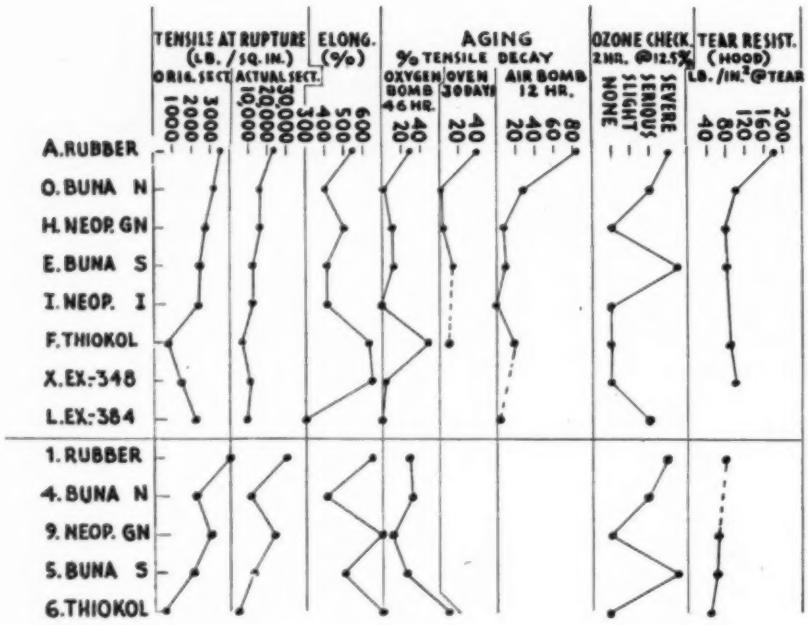


FIG. 1. Summary of conventional rupture and aging data for the two groups of motor support stocks.

to the right. The heavy connecting lines are included to facilitate comparison of different properties. The first four stocks *A*–*E* (high black stocks) correspond to the first four below the heavy horizontal line (low black stocks). Neoprene *I*, a recently announced solvent-resistant polymer, has been added as well as the experimental stocks EX.-348 and EX.-384. The latter two stocks will not be described. They have been added only because of their rather unusual physical properties.

The tensile strength calculated on the actual section at rupture is seen to give no information not given by the conventional tensile on the original section. This is not always true and should be considered important only in that the usual criterion for degree of pigment reinforcement in rubber stocks (tensile on actual section) does not add to our knowledge in comparing relative properties of these rubber and synthetic stocks. Tear resistance (last column) is more revealing as it indicates a marked inferiority in this respect on the part of the synthetic stocks. Again we must realize that, although it is probably desirable to improve the tear resistance of the synthetics, we must not be influenced too much by our past experience with rubber where high tear resistance is very important. Possibly, other properties inherent in the synthetics may more than counterbalance this apparent deficiency.

The aging data are very important as they indicate marked superiority over rubber for Neoprene under all three conditions and for Buna N and Buna S with high black loading. For the information of those not familiar with rubber technology, the oxygen bomb test subjects strips of stock to a temperature of 70°C at 300 lb./in.² oxygen pressure. The oven is operated at 70°C. The air bomb is maintained at about 125°C and 80 lb./in.² air pressure.

The ozone aging results are very interesting and definite, although plotting qualitative data of this type can hardly be considered practical. A photograph of the actual strips extended to 50 percent elongation in order to show the checking clearly is given in Fig. 1*A*. Here we find Buna N and, particularly, Buna S checking very badly, whereas they showed a marked resistance to oxygen and heat in the bomb and oven tests at zero elongation. In the ozone test, the strips were held at 12.5 percent elongation, which is considered to be in the range where maximum checking of rubber occurs. A commercial ozone generating device was used in the ozonizing chamber, the temperature of which was maintained at about 32°C. The frame holding the stretched strips was rotated slowly to insure

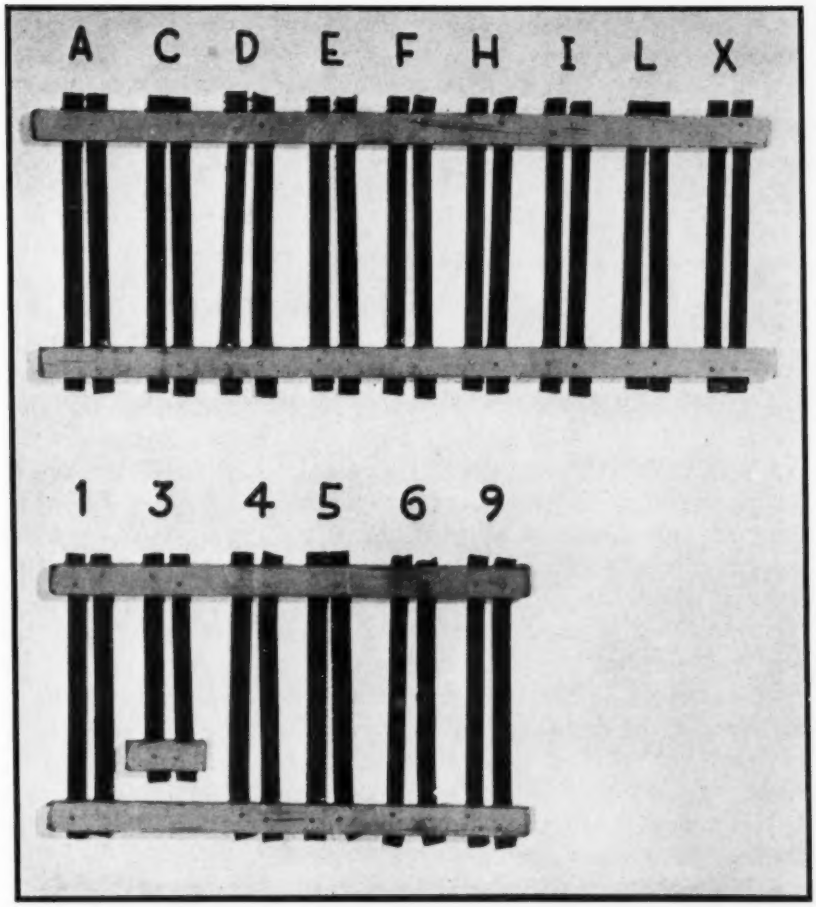


FIG. 1A. Ozone-aged strips.

uniform treatment. Neoprene and Thiokol stocks showed no ozone checking whatever. Thus, Thiokol may be used in applications where ozone resistance is essential but where high resilience, tensile, and heat resistance are unimportant. Neoprene with good mechanical and excellent aging, and ozone resisting characteristics appears to show considerable promise as an improvement over natural rubber in many applications in spite of its higher cost. Its use in airplane tires, for example, will possibly increase because of its resistance to high ozone concentrations in the upper atmosphere.

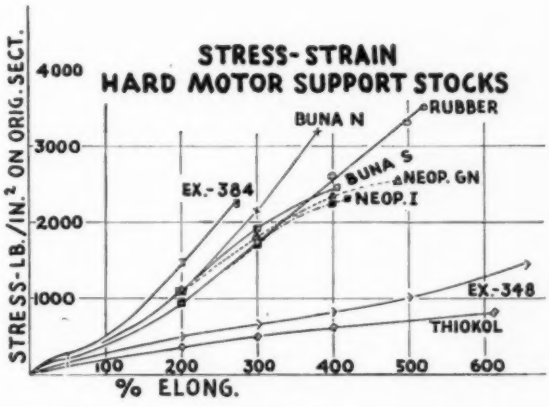


FIG. 2. Stress-strain—hard motor support stocks.

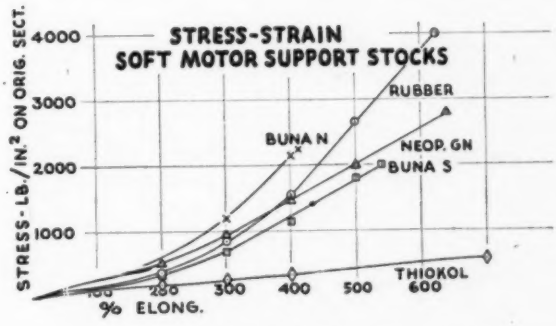


FIG. 3. Stress-strain—soft motor support stocks.

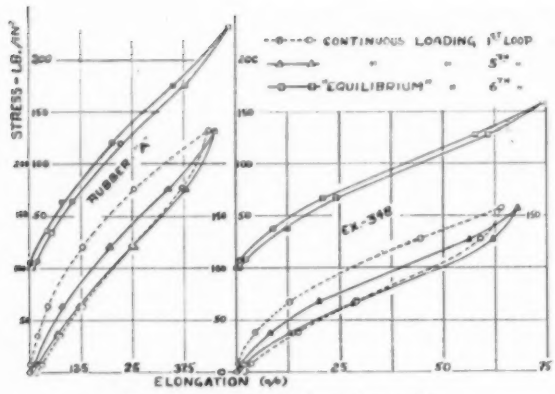


FIG. 4. Hysteresis-low elongation.

Stress-Strain Curves

No discussion of rubber would be complete without the appearance of stress-strain curves, whatever be their significance. The curves for the high black series of motor support stocks are shown in Fig. 2. The curves are all of the characteristic "rubber type" except for what appears to be "pigment overload effect" at high elongations in the cases of the Neoprene and Buna S. This effect has been observed with rubber stocks of different compounding, however, and thus merits no further comment. It disappears in the curves for the low black stocks given in Fig. 3. It should be remarked that these curves were obtained with a standard Scott testing machine for elongations of 200 percent and greater. Points at 50 percent elongation were obtained by a continuously increasing dead weight loading method and are sufficiently accurate to indicate the manner in which the curves leave the origin.

Two sets of low elongation stress-strain curves are shown in Fig. 4. The procedure used consisted in progressively loading and unloading the test strips with the same set of weights so that five complete hysteresis loops were obtained. Only the first and fifth loop are shown for reasons of simplicity. In both the case of rubber and of the synthetic EX.-348 the difference between the fourth and fifth loop was unobservable with the accuracy employed. The sixth loop was obtained by the so-called "equilibrium" method, previously studied by a number of workers, notably Gerke.[2] Here the test strip was allowed to retract completely after each loading and unloading and then the dead weight load was moved up and down about the equilibrium position through an amplitude of about 50 percent of the elongation for the load in question. A further decrease of about 100 percent in the hysteresis loop area is seen to have taken place upon application of this method of loading. The most striking feature of these two sets of curves is their similarity. In spite of this similarity, a rebound test, where a 0.5-in. steel ball was dropped from a

[2] R. H. Gerke, Ind. Eng. Chem. **22**, 73 (1930).

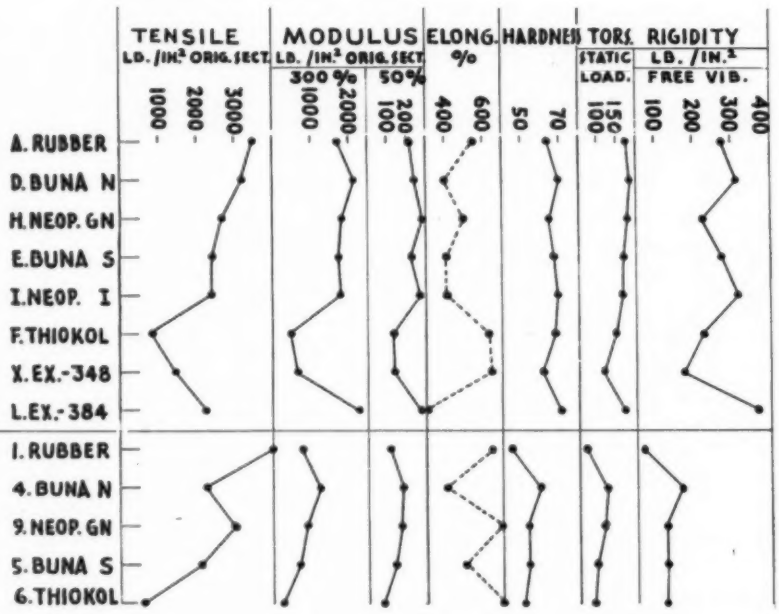


FIG. 5 Measurements of elastic resistance to deformation.

height of 1 meter on 0.75-in. slabs of these stocks, gave 42 percent rebound for the rubber stock and only 7 percent for EX.-348. This rather extreme disagreement between static and impact data clearly illustrates that great caution must be observed in applying common "rubber tests" to the synthetics.

Elastic Properties

A chart giving several measurements of elastic resistance to deformation is shown in Fig. 5. The tensile strength and elongation are again included for reference. The 300 percent and 50 percent modulus values were measured by methods already described. Hardness figures were obtained with the Shore durometer. The torsional rigidity or modulus in shear was obtained by a special autographic machine developed in the Firestone laboratories by W. F. Bartoe. This machine is essentially a high frequency torsion pendulum with extremely low friction and windage corrections. Space hardly permits further description. Suffice it to state that the natural frequencies of the various stocks in this machine varied from 2 to 6 sec.$^{-1}$.

Examination of this chart reveals a surprisingly good correlation between hardness, static rigidity, and "dynamic" rigidity obtained in free vibration. The 300 percent and 50 percent moduli also correlate with each other and with the hardness and rigidity values in a general manner, provided the hard group of stocks is not compared against the soft group. In the light of experience with rubber stocks of radically different compounding and state of cure, this singularly good correlation, which appears to minimize the practical value of dynamic measurements at low strain, was unexpected. Furthermore, these values of torsional rigidity for the high black series have been found to agree quantitatively with the values of Young's modulus $\times\frac{1}{3}$, obtained from the natural frequencies (14–20 sec.$^{-1}$) in forced compressional vibration under a static load of 50 lb./in.^{2}. This agreement was still more surprising since no slippage of the contact faces of the compression samples occurred. However, the compressional strain was less than 10 percent in all cases. The authors wish it clearly understood that they wish to defer any general conclusions on this matter until more work has been done.

Hysteresis, Fatigue, and Permanent Set

We have already discussed hysteresis loss in connection with low speed tensile tests and ball rebound for two stocks. The results of these and other tests on all the stocks are plotted in the chart (Fig. 6). In this chart, the hysteresis loss values as given by the first cycle of tension loading are compared with those obtained by the falling ball rebound test, and from the hysteresis

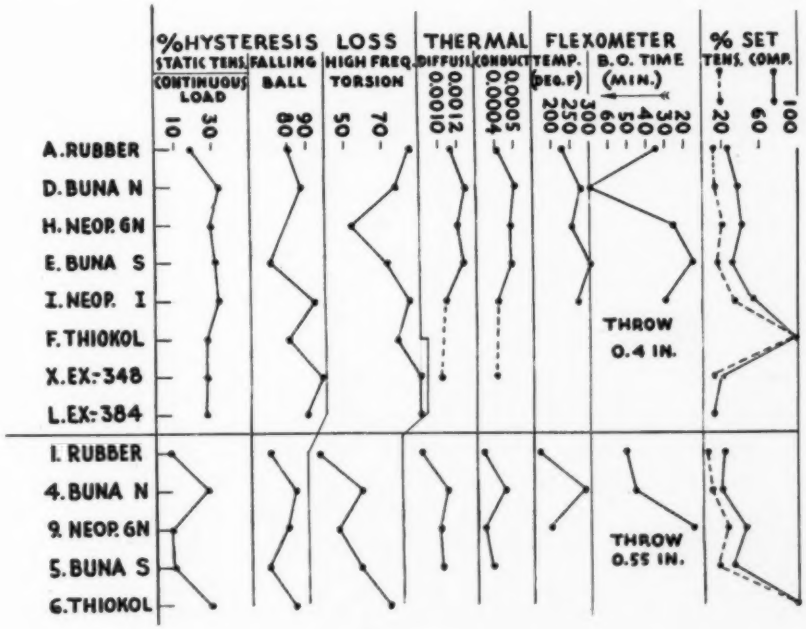


FIG. 6. Hysteresis, thermal conductivity, and permanent set.

loss per cycle, calculated from the rate of damping in free vibration. The latter was measured by the machine, previously mentioned, with which torsional rigidity was measured. We see that the tensile hysteresis measurements do not correlate satisfactorily with the falling ball results and still less satisfactorily with the high frequency free-vibration data. From a quantitative viewpoint, of course, none of these results obtained by different methods agree, nor should they.

"Blowout time" and "equilibrium running temperature" measured with the Firestone flexometer[3] are also plotted in this chart. With this machine, rubber blocks under dead load are deformed in simple shear with a shear stress vector which rotates at 800 r.p.m. in the horizontal plane. The loading anvils of the machine are of Bakelite in order to inhibit heat loss from the rubber. This machine was developed with the aim of measuring the resistance of rubber stocks to blowout under exaggerated conditions of load and throw. The load or throw of the flexometer can be reduced so that the rubber blocks can be raised to and held at an equilibrium temperature which appears to be a function of the rate of heat generation and conduction of the stock. The time required for "blowout" is a composite index involving heat generation, thermochemical stability, and possibly permanent set. For the high black stocks of this chart, it is painfully obvious that none of the various hysteresis values would allow dependable predictions of "running temperature." In the case of the three low black stocks, however, all of the hysteresis indices appear to be very satisfactory in this respect. Values of the thermal conductivity vary in a manner exactly the opposite of that necessary to explain away the lack of correlation of the hysteresis values with "running temperatures" for the high black stocks.

Comparison of "running temperature" and blowout time yields some very interesting conclusions. Buna N runs for a considerably longer time before blowout than rubber does in the high black stocks but generates a higher "running temperature" than rubber in both series. It exhibits about the same resistance to blowout as that of rubber in the low black series. Thus, Buna N appears to resist blowout rather well in spite of its higher "running temperature." The Buna S stock runs at the highest temperature and appears inferior to rubber in "blowout resistance." As a final link in this chain of physical discords, Neoprene runs only slightly better than rubber but has a much shorter blowout time in the case of the low black stocks. It should be pointed out that the "blowout resistance" and "running temperature" are, to a considerable extent, dependent on the compounding of the stocks and, consequently, the results must not be interpreted as being entirely characteristic of the base polymers.

The permanent set values of Fig. 6 were obtained as follows: For compression set, the cylindrical samples were compressed to 25 percent of their original height and held at 70°C for 20 hours. They were then removed from the oven and immediately released and measured. In the tension tests, dumbbell samples were extended to 100 percent elongation and held at 70°C for 20 hours. They were then removed from the oven and cooled for 2 hours before release. After release, a period of 2 hours elapsed before measurement of permanent elongation. The two types of measurement agree very well in eliminating Thiokol as a substitute for rubber under load. The Buna stocks appear somewhat superior

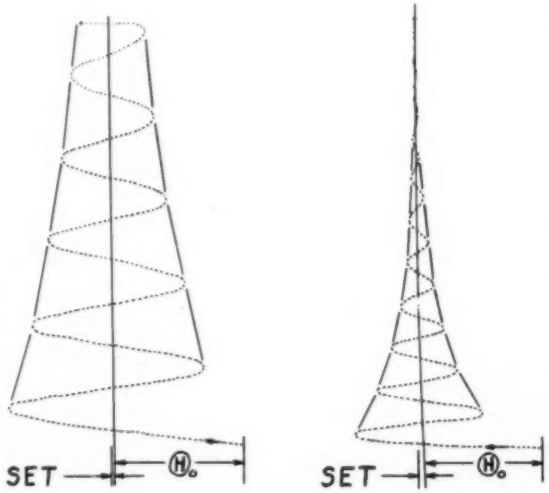


FIG. 7. Typical free vibration records. Initial maximum shear strain 0.2.

[3] L. V. Cooper, Ind. Eng. Chem. Anal. Ed. **5**, 350 (1933).

to the Neoprene stocks but slightly inferior to the rubber stocks.

Returning briefly to the subject of hysteresis measurements, tracings of typical free vibration records for rubber and Buna N in the low black series are shown in Fig. 7. These damped curves probably illustrate more clearly than any figures or charts that, though Buna N may be a satisfactory substitute for rubber because of its overall service characteristics, it is certainly not its equivalent in detailed physical properties.

Tensile Strength at Elevated Temperature

The decay of tensile strength with increasing temperature for five stocks of the high black series is shown in Table III.[4] It is seen that both the Bunas and the Neoprenes lose a much greater fraction of their tensile strength than does rubber when the temperature is raised to 70°C. The importance of this apparent deficiency on the part of the synthetics is not as yet known. This question would appear to hinge on the importance of tensile strength at room temperature as a quality index, an index used universally for many years by rubber technologists with considerable success. When it is noted that Buna N is exceptionally resistant to blowout in the flexometer test, which certainly approximates service conditions more closely than the tensile test, the relevance of high tensile strength for the synthetics, at least at high temperatures, appears

TABLE III. *Tensile vs. temperature—hard motor support stocks.*

	RUBBER	BUNA N	BUNA S	NEOP. GN	NEOP. I
Tensile at 27°C (lb./in.²)	3500	3050	2200	2675	2400
Tensile at 70°C (lb./in.²)	3075	1600	1125	1825	1575
Tensile decay (percent)	12	47	49	32	34

doubtful. The opinion expressed by some workers that the rubber tensile test is not a true measurement of tensile strength but rather a measure of tear resistance appears to be substantiated by these results when the low tear resistance of the synthetics at room temperature is considered.

[4] These tensile strength measurements at 70°C were obtained through the kindness of M. F. Torrence of the E. I. du Pont de Nemours Co.

Swelling Tests

One of the major uses for synthetic rubber in the past has been in the fabrication of parts which are to be used in contact with oil or gasoline. In

TABLE IV. *Swelling: Percent increase in weight—7 days.*

	GASOLINE	BENZOL	PARAFFIN BASE OIL	NAPHTHENIC BASE OIL	WATER
Rubber	76	130	69	104	2.6
Neoprene GN	14	107	6.3	14	15.0
Neoprene I	6.3	90	0.3	1.7	1.9
Buna N type	9	118	0.8	1.9	2.0
Buna S type	48	145	36	59	1.5
Thiokol	0.4	50	0	0	7.9

Table IV are plotted the results of comparative tests in high test gasoline, benzol, SAE-30 oil, and water. The results recorded are for a seven-day test period in all cases. Data for the complete curves were obtained over a 28-day swelling period but, because the relative swelling values remained nearly constant, the 7-day results give all the essential information. The test was carried out at 25°C in the case of gasoline and benzol, and at 70°C in the case of the other liquids. Increase in weight was measured and is recorded. The dimensions of the sample and general method were those prescribed by the A.S.T.M. except as noted above.

The results are essentially the same as those reported previously in the literature. Thiokol is apparently the most resistant to gasoline, benzol and oil. Buna N type is somewhat more resistant to gasoline and oil than Neoprene GN. The experimental Neoprene polymer is apparently a definite improvement over the GN polymer in swelling resistance.

Synthetic Rubbers in Tires

The outstanding desirable properties attainable with certain of these synthetics have been shown here and elsewhere to be resistance to solvents and stability at elevated temperatures. The matter of abrasion resistance has not been discussed from a laboratory standpoint since no entirely satisfactory abrasion test has been developed for rubber although much effort has been expended in that direction. In the case of tires, controlled road tests are the only reliable index of

abrasion resistance. Thus, after a compound has been developed which has a reasonably balanced set of physical properties such as tensile strength, modulus, and hysteresis loss, and which stands up well under the numerous laboratory fatigue and aging tests, it is incorporated in tires and a service test made. Various companies in the rubber industry have carried out fairly extensive tests with synthetic rubber tires. Our conclusions on passenger car tires, from those tests carried out by our own organization may be of interest. On test cars we have found Buna S to give wear equivalent to that of our best rubber treads. Under ideal conditions of compounding and service, Buna N has proved somewhat better. However, the use of Buna N without modifications in tires appears hopeless owing to processing and fabrication problems. Neoprene has given results equal to those of rubber and Buna S. Abrasion resistance, of course, is only one property of importance in tire service. Resistance to tear, ozone, etc., are also very important. The opinion can be given that, in case of emergency, rubber could be replaced with a synthetic in passenger tires from the quality standpoint. In the case of truck and bus tires, however, where the conditions of service are much more severe, we do not feel that we have sufficient data to make a similar optimistic prediction.

One of the major problems of a move to synthetics on a large scale has been passed over very lightly in the more popular articles. This relates to processing. The statement often appears that the synthetics process just like rubber on rubber machinery. On the contrary, it has been our experience that each of these materials has unique processing characteristics and requires special processing treatment. For large scale production, either production must be slowed down appreciably or equipment modifications made.

Conclusion

The rather complicated relationships between the various physical or pseudo-physical properties discussed in this paper might seem to those unfamiliar with rubber technology to constitute an almost hopeless maze of contradictory evidence of little possible use in evaluating the new synthetic materials. The critical rubber technologist, however, would not be too greatly disturbed by these contradictions for a similar situation once existed in regard to natural rubber and still exists to a limited extent in this highly developed field. In the early history of the rubber industry, indeed, it seemed quite natural to adapt the physical test concepts of the metals industry to the new material, rubber, in spite of its strikingly different physical properties. In the subsequent period in which improvements in serviceability followed one another in rapid succession, it is not surprizing that relatively little progress in physical evaluation methods was made and rubber compounding developed more as an art than as a science. At the present time, with service conditions constantly becoming more severe, the value of the scientific approach, coupled with the art, is at last achieving success and recognition.

In the case of the new synthetics, fortunately, a much better physical background is available than was the case in the early days of rubber manufacture. The new materials must be fitted to service conditions which, though severe, at least are known to a certain extent. Furthermore, the synthetics are very similar to rubber in outward appearance and possess many of its physical properties. Thus, if reasonable care is taken to modify the physical testing methods already available for rubber stocks and to devise new methods when necessary, progress in application of the synthetics should be rapid. The data presented in this paper and elsewhere certainly indicate that great care must be taken in their evaluations. Possibly our whole concept of the structure of rubber will undergo a change when we have finally learned the essential physical properties of the synthetics. Finally, we may come to understand rubber through the study of these other substances designed to supplant it.

In conclusion, the authors wish to express their gratitude for the invaluable help, in obtaining the physical data of the paper, rendered by J. E. Whittenberg, I. B. Prettyman and E. E. Hanson of the Firestone research group. The helpful cooperation of Mr. L. V. Cooper, Manager of the physical testing laboratory, is also very much appreciated.

Resumés of Recent Research

Transmission of Infra-Red Radiation Through Fog

It appears to have become the accepted conclusion that the intensity of infra-red rays after passing through a moisture-laden atmosphere is substantially the same as that of light rays or that the difference is too slight to be of practical value.

To determine the correctness of the above conclusion, tests[1] were made with a radiometer held at the focus of a parabolic reflector so arranged that different filters could be rapidly interposed in the path of the beam between the reflector and the radiometer. These filters were chosen so as to divide the spectrum of the incoming radiant energy into three bands. The radiometer measured the energy received in each of these bands as well as that when no filter was in the path. These four measurements could be made easily in less than one minute and thus tended to insure that atmospheric conditions were substantially the same.

The following table shows the energy received on two days. Column 1 gives the energy received on one of the clearest days and column 3 similar energy readings when the path of the beam was heavily laden with moisture.

Filter	1 Reading	2 %	3 Reading	4 %
No filter	530	100	190	36
Water (band I)	26	100	2	8
Red glass (band II)	255	100	87	34
MgO (band III)	250	100	110	44

It is to be noted that the observations were recorded in percentages of the standard—column 1—for each band. If the percentages of transmission for all bands were the same, the plots would be straight lines from the 100 percent point of origin. Band I was made the basis of comparison as it most nearly represents the visible portion of the spectrum plus about that to which the photoelectric cell is responsive. Figure 1(a) shows that, when the atmosphere was so laden with moisture that the intensity of the radiation within band I was only 36 percent of that which had been received on the clearest day, the intensity of the radiation of the rays of longer wave-lengths, i.e., those in band II and III, at the same time and under the same conditions was about 60 percent of that found on the clearest day. Likewise, when the radiation within band I was so small as to make reliable readings impossible, the received radiation of band II and band III was about 34 percent and 44 percent of that which had been received under similar atmospheric conditions.

The only conclusion that can be reached from the above figures is that: *Of the radiations from a hot source the longer rays suffer less attenuation in passing through a fog than the shorter visible or nearly visible rays.*

It is our belief that the reason for the difference between our conclusion and that of most earlier

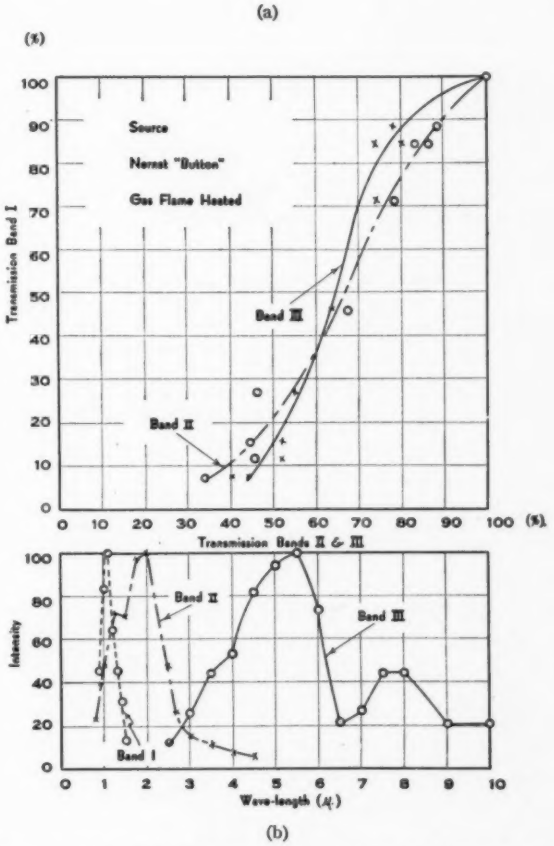


Fig. 1. (a) Results of Boston tests. (b) Spectra of filter bands from hot button of Nernst materials.

[1] P. N. Smith and H. V. Hayes, J. Opt. Soc. Am. **30**, 332 (1940).

investigators lies in the fact that the Hayes Radiometer, apart from its great sensitivenesss has been given a very wide field of vision, so that it will be actuated by the energy scattered by the suspensoids as well as those coming directly from the source.

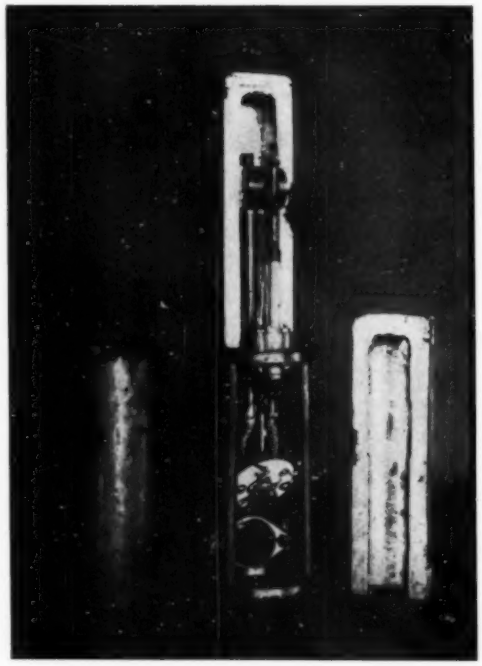
Directional Dependence of Electrical Conductivity The well-known fact that the electrical conductivity depends on direction in metallic crystals has received very little attention since the development of the modern quantum theory of solids. The fundamental equations of the theory of conductivity contain anisotropic terms which would obviously lead to a directional dependence, but ordinarily these factors are replaced by appropriate isotropic terms, since for most investigations the anisotropies are not of interest and lead to apparently useless complications.

In the present work[1] the fundamental equations are developed in a form which is sufficiently general to include the anisotropies. Certain interesting characteristics of the electron-lattice interaction responsible for the resistance are emphasized. In particular, the importance of transverse lattice waves is stressed. Many published treatments of the conductivity deal with monovalent metals and with good reason arrive at the conclusion that only longitudinal lattice waves play a rôle. However, the restricted validity of the conclusion can all too easily be overlooked. The present study makes plausible the conclusion that for many metals the transverse waves are the more significant, especially at low temperatures.

A large portion of the work is devoted to a calculation of the directional dependence for certain models, results being obtained for both high and low temperature conditions. The treatment as a whole makes it very evident that the effect is essentially complicated, a variety of inter-related factors playing significant rôles. It does not seem possible at present to make even very rough estimates of the directional dependence for real metals.

[1] This note is a resumé of a recent *Physical Review* article: E. M. Baroody, Phys. Rev. **58**, 793 (1940).

The Heat of Fission of Uranium Perhaps the most striking feature of the recently discovered process of nuclear fission is the enormous amount of energy that is liberated by it. In the November *Physical Review* a paper by M. C. Henderson[1] reports a direct measurement of this energy. The apparatus consisted of a resistance thermometer to measure the rate of heat evolution in a 13-g sample of metallic uranium and an ionization chamber and pulse amplifier combination to measure the number of fissions occurring in a 54-microgram sample. The two samples were inside the same shield in the same atmosphere of slow neutrons, and the calculation of the heat liberated per fission was made, in principle, by dividing the heat by the number of fissions and by the ratio of the masses of the samples.



Apparatus used to determine the heat produced in the fission of uranium.

The corrected result is 177 Mev ±1 percent, an average of thirteen runs. This figure is to be compared with two others: a theoretical value of approximately 200 Mev that can be calculated from the masses involved, and also the experimental figure of 163 Mev of Kanner and

[1] M. C. Henderson, Phys. Rev. **58**, 774 (1940).

Barschall,[2] obtained by counting the number of ions produced by a pair of recoiling fission particles and multiplying by the energy required to form a single pair of ions. The difference between calculated and measured values is explained[3] by the fact that much of the energy in the fission process must go to excite the residual nuclei. Some of this excitation will be lost as neutron and gamma-ray emission, neither of which are caught by the calorimeter. The difference between the heat measurement and the ionization method is explicable because the calorimeter catches practically all the beta-rays, even when they have a radioactive half-life of several minutes. The difference corresponds to 8 beta-rays each having about 1.7 Mev, which are reasonable figures, and the experimental results are thus in good agreement.

[2] M. H. Kanner and H. H. Barschall, Phys. Rev. **57**, 372 (1940).
[3] N. Bohr and J. A. Wheeler, Phys. Rev. **56**, 426 (1939).

Columbium-Iron Alloy Recent investigations have indicated that alloys containing a finely dispersed stable phase are the strongest metals for use at temperatures of 1100°F and above. An alloy of this kind has been produced by adding small amounts of columbium to iron.[1] No carbon is used in this alloy; the iron contains the columbium as a finely dispersed stable compound of iron and columbium.

Room-temperature tensile tests, creep tests, and rupture tests, all in accordance with the approved A.S.T.M. and similar standards, have been conducted on the columbium alloy, and results compared with results of similar tests on steels. Samples consisting of three percent columbium and ninety-seven percent iron revealed exceptionally good rupture strength at 1100°F, a temperature which is not yet commercially used, but which is being approached by modern high temperature, high pressure steam turbines. The new alloy may make it possible, therefore, without excessive cost, to extend further the temperature at which steam turbines are operated. In fact, the columbium-iron alloy is reported to be outstanding in all respects for use at the specified temperature, considering its cost, ease of production, machinability, and other properties.

The columbium-iron alloy has been produced in two different ways: (1) The correct proportions of the powdered metals have been mixed, then sintered, and finally, as a fused mass, swaged into a metal capable of being heat-treated and machined in the usual way; and (2) the alloy has been cast and forged. The cast alloy equals the sintered material in its properties, so that commercial production of the alloy is not expected to offer difficulties.

Up to the present time only a small tonnage of columbium has been produced annually, but it is expected that the supply could easily be increased with increased demand.

[1] Alloy announced by R. E. Parker, General Electric Research Laboratory, Schenectady, New York, at the annual meeting of the American Society for Metals in Cleveland, October 21, 1940.

Contributors to This Issue

H. Mark

Herman Mark received his Ph.D. degree from the University of Vienna, and, at the time of the invasion of Austria, he held the position of Director of the Chemical Institute at that University. He was for a time Research Manager of the Canadian International Paper Company, Hawkesburg, Ontario. Dr. Mark is now Adjunct Professor of Organic Chemistry at the Polytechnic Institute, Brooklyn, New York.

Gregory (Stephen) Timoshenko has been since 1939 Assistant Professor of Electrical Engineering at the University of Connecticut, where he is in charge of the work in electrical measurements and illuminating engineering. Dr. Timoshenko, a native of Russia, received his Ph.D. degree from the University of Michigan in 1932.

William C. Sears received a B.A. degree from Ohio Wesleyan University in 1931, and the M.Sc. and Ph.D. degree from Ohio State University in 1932 and 1937, respectively. Since 1937 he has been a research physicist with the B. F. Goodrich Company, investigating the electrical properties of rubber and synthetic polymers.

J. W. Schade

James Walter Schade has been associated with the B. F. Goodrich Company since 1909 and became Director of Research for that company in 1925. Mr. Schade is a graduate of Cornell University, and was employed with the J. T. Baker Chemical Company of Phillipsburg, New Jersey, and the Industrial Laboratories, New York City, before joining the Goodrich staff.

W. C. Hahn received his B.S. degree at the Massachusetts Institute of Technology in 1923. Following a student engineering course at General Electric, Mr. Hahn was sent to the company's Chicago office where he worked from 1924 to 1932. Since 1933 he has been in the Engineering General Department at the Schenectady Works.

G. Timoshenko

W. C. Sears

Stuart H. Hahn is a mechanical engineer in the Physical Research Laboratory of the B. F. Goodrich Company, a position he has held since 1928. Mr. Hahn received his B.S. degree from Carnegie Institute of Technology in 1927 and spent a year after his graduation with the Timken Roller Bearing Company.

W. C. Hahn

O. R. Fouts

J. H. C. Smith

S. H. Hahn

John N. Street was Research Chemist and Assistant Director of Chemical and Physical Research for the Firestone Tire and Rubber Company from 1926 to 1936, in which year he became Director of Chemical and Physical Research there. Dr. Street received his M.S. degree from the University of Syracuse in 1923, and his Ph.D. degree from the University of Wisconsin in 1926.

The following contributors have received mention in earlier issues of the *Journal of Applied Physics:*

J. H. Dillon, p. 251, Vol. 11, No. 4, 1940.
James E. Field, p. 562, Vol. 10, No. 8, 1939.

James H. C. Smith is a staff member of the Division of Plant Biology, Carnegie Institution of Washington, located at Stanford University, California. He is engaged in research on the process of photosynthesis, particularly the absorption and utilization of carbon dioxide by leaves.

Omer R. Fouts is Assistant Professor of Physics at the University of Akron. He received his B.A. degree from Wittenberg College in 1920 and his M.A. from Ohio State University in 1925. He has also studied for several terms at the University of Michigan.

Here and There

Research Fellowships Available

Five new appointments of Westinghouse Research Fellows will be made in the spring of 1941, according to that Company's recent announcement. The aims of the Westinghouse Electric and Manufacturing Company in establishing the fellowships are: (1) "to make a worthwhile contribution to the development of the fundamental sciences on which modern industry is based," and (2) "to enable a group of able investigators to become familiar with the scientific problems confronting the electrical industry." The Westinghouse Research Laboratories include the following six departments: mechanics, electromechanics, electrophysics, chemical and metallurgical, magnetic, and insulation. The work of the Fellows will be carried on within the appropriate department under the general supervision of Dr. E. U. Condon, Associate Director.

Appointments are made for a period of one year, and Fellows are eligible for one reappointment for a like period. Applications for the post-doctorate fellowships should be made on available forms and should be addressed to the office of the Manager, Technical Employment and Training, Westinghouse Electric and Manufacturing Company, 306 Fourth Avenue, Pittsburgh, Pennsylvania. To receive consideration applications must be received by February 15, 1941.

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Company to Build in Brooklyn

The Glyco Products Company, Inc., manufacturer of chemicals, has approved plans for a new building to be erected in Brooklyn, New York. It is anticipated that operations will be commenced on or about December 15, 1940. The Company's expansion project will consist of three sections; the administration building and research laboratory, both to be located at 228–236 King Street, and the shipping and receiving departments, to be housed at Pioneer Street.

Electron Microscope Fellowship Awarded

Dr. Thomas F. Anderson, known in the scientific world for his research in biology, surface chemistry, and spectroscopy, has been named by a committee of distinguished scientists to receive the RCA Electron Microscope Fellowship. The terms of the Fellowship provide for investigation of biological problems with the RCA electron microscope and for experimentation leading to the development of techniques for obtaining the fullest benefits from that instrument. The work is being carried on at the RCA Research Laboratories in Camden, New Jersey.

Dr. Anderson received his Ph.D. degree in 1936 from the California Institute of Technology. One year of his graduate work was done in Munich. Since receiving the Ph.D. degree he has done scientific research work at the University of Chicago and the University of Wisconsin. He has published a total of 13 technical papers on a wide variety of subjects.

Dr. Stuart Mudd of the University of Pennsylvania's School of Medicine is chairman of the RCA Fellowship Committee which named Dr. Anderson for this award. Other members of the committee are Dr. M. Demerec, Station of Experimental Evolution, Carnegie Institution of Washington; Dr. J. H. Kempton, United States Bureau of Plant Industry; Dr. C. W. Metz, Department of Zoology, University of Pennsylvania; Dr. W. M. Stanley, Rockefeller Institute for Medical Research, Princeton, New Jersey; Dr. Caryl P. Haskins, Haskins Laboratories; and Dr. V. K. Zworykin, RCA Research Laboratories.

★

New Office Opened

The opening of a branch office in Rochester, New York, is announced by the Ward Leonard Electric Company. The new office, located in the Lincoln Alliance Bank Building, 183 Main Street East, will be managed by Mr. J. K. Savage, Sales Engineer.

Harvard University Physics Department Changes

Professor E. L. Chaffee has taken over the directorship of the Cruft Laboratory at Harvard University, following the retirement of Professor G. W. Pierce, according to a recent announcement in *Science*. Professor E. C. Kemble succeeds Professor F. A. Saunders as Chairman of the Department of Physics, a post which Professor Saunders recently resigned. Announcement is made also of the retirement of Professor N. H. Black.

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Ohio Section of American Physical Society Convenes

A Symposium on the Physics of Rubber was held in connection with the third meeting of the Ohio Section of the American Physical Society, which took place at the University of Akron, Akron, Ohio, on Friday and Saturday, October 11 and 12. The mid-year meeting of the Ohio Section will be held on Saturday, March 29, 1941, at Muskingum College, New Concord, according to Richard H. Howe, Secretary-Treasurer of the Section. Contributed papers will be solicited for this meeting.

During the Akron meeting tours were taken through the aeronautical experimental laboratories of the Guggenheim Airship Institute and through the plant of the B. F. Goodrich Tire and Rubber Company. The Friday evening address, following a banquet, was given by Professor P. Debye, Cornell University, who spoke on "Physical methods for investigating the structure of molecules."

★

Company Expansion Announced

The second major expansion of the Wheelco Instruments Company since its organization in 1935 has been recently announced. The Company's general offices have moved to larger quarters, permitting substantial increases in personnel and equipment, according to the announcement. The general offices are located at 2001 South Halsted Street, and the plant at 1929–33 South Halsted Street, Chicago, Illinois.

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Calendar of Meetings

February

21–22 American Physical Society, Cambridge, Massachusetts

April

4– 5 Southeastern Section of American Physical Society, Vanderbilt University, Nashville, Tennessee
7–11 American Chemical Society, St. Louis, Missouri
16–19 The Electrochemical Society, Inc., Cleveland, Ohio

May

1– 3 American Physical Society, Washington, D. C.
5– 7 Acoustical Society of America, Rochester, New York

June

20–21 American Physical Society, Providence, Rhode Island
23–27 American Association for the Advancement of Science, Durham, New Hampshire

Two Schools Combine

The trustees of Armour Institute of Technology and of Lewis Institute, Chicago, Illinois, announce the consolidation of these institutions to form Illinois Institute of Technology having as its divisions Armour College of Engineering, Lewis Institute of Arts and Sciences, the Graduate School, and Armour Research Foundation. This consolidation became effective in September.

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Instrument Booklets

Laboratory Microscopes, Types A–B–C, 15-page catalog No. D–185, of the Bausch and Lomb Company, describes new models designed to replace the Bausch and Lomb Type H microscopes. The new models are illustrated and the specifications of each listed in table form. In this booklet the outfits fitted with quadruple nosepiece and 3.2× objective are regularly catalogued. The manufacturers point out that this is in line with current practice where low power searching and general survey precede high power examination.

A "Sylphon metal bellows data sheet," on which perspective users of the instrument can provide the manufacturer with pertinent information on the specific type desired, accompanies the recent leaflet, *The Sylphon Bellows*, published and distributed by The Fulton Sylphon Company, Knoxville, Tennessee. Schematic drawings and characteristics of a few standard brass single ply bellows are furnished in the leaflet.

Electrical Measuring Instruments for Research, Teaching and Testing contains 64 pages of descriptive material and current prices on the products of the Leeds and Northrup Company, 4991 Stenton Avenue, Philadelphia, Pennsylvania. For more complete descriptions and much supplementary information about the instruments listed in this Catalogue E, the reader is referred throughout the text to a wide variety of catalogs and bulletins which treat instruments or assemblies as such, or apparatus for specific uses.

Cathode-Ray Indicating Instruments for All Purposes is the title of Catalog B, published recently by the Allen B. Du Mont Laboratories, Inc., Passaic, New Jersey. The scope of the 68-page booklet is described in the introduction: "The pages of this catalog list the latest contributions of this laboratory to the oscillograph field." Among these will be found an instrument to satisfy practically every oscillographic requirement, from rough, field applications to equipment designed for exacting laboratory determinations.

Apparatus for determining carbon by the combustion method is shown on the cover of a recent issue of *The Burrell Technical Announcer*, published by the Burrell Technical Supply Company of Pittsburgh, Pennsylvania.

Innovations in Instruments

Photoelectric Cells

The Luxtron Photoelectric Cells, manufactured by Bradley Laboratories, Inc., 82 Meadow Street, New Haven, Connecticut, offer comparatively low variations in electrical characteristics, according to the manufacturers. These cells are of the selenium barrier layer dry disc type and are supplied uncased or mounted in a moulded casing as a protection against corrosive vapors. Representative electrical characteristics for the Luxtron Photo-Electric Cells are given in the form of graphs in Catalog No. 101, issued by the Bradley Laboratories recently. Curves showing photo-current characteristics with several external resistances, temperature variation of photo-current at various illuminations and external resistances, potential-illumination characteristics, fatigue characteristics, and relative spectral response, for various cell models are included in the catalog.

Potentiometer-Pyrometer

The portable potentiometer-pyrometer, Model 70–PO, manufactured by J–B–T Instruments, Inc., 441 Chapel

Street, New Haven, Connecticut, is shown in the accompanying photograph. Measuring sub-zero or 3000°F, with potentiometer independence of lead resistance and fewer balancing operations, this model is of importance in many fields, according to the manufacturers.

Extruded Plastic Tubing

Extruded plastic tubing known as Irv–O–Lite XTE–100, which maintains all its characteristics at a continuous temperature of 176°F, is announced by the Irvington Varnish and Insulator Company, 24 Argyle Terrace, Irvington, New Jersey. This tubing has a dielectric strength when dry of 750 volts per mil and, after 24 hours' soaking in water, of 400 volts per mil. Its tensile strength is 2000 pounds per square inch.

Commercial "Non-Reflection" Surfaces

The production on a commercial basis of low reflecting surfaces on glass by high-vacuum distillation of metallic fluorides has been recently announced by the National Research Corporation, 100 Brookline Avenue, Boston, Massachusetts. The technique employed involves the coating of carefully prepared glass surfaces with suitable materials such as magnesium or calcium fluoride. The coating is deposited by distillation under an extremely high vacuum, that is, a pressure of less than 0.000001 mm of mercury, and the deposition must be controlled so that its thickness is one quarter the wave-length of light. As a result of this treatment a single lens which normally transmits only 92 percent of all light that strikes it may be made to transmit about 99 percent; eight lenses in series which together normally waste half of all the light that is received, have a transmission of 92 percent after treatment.

Immediate applications of this process suggest themselves in connection with the design and manufacture of optical apparatus. The treatment of range finders, binoculars, telescopes, bomb sights, and similar equipment may be of interest also. In aerial photography, for example, questions of "resolving power" of the large and complicated lenses are particularly important in order that the maximum amount of detail may be recorded. Here another advantage of "non-reflecting surfaces" becomes apparent; namely, the elimination of multiple reflections within the camera lens.

The process of coating "non-reflecting surfaces" by evaporation of certain chemical salts under high vacuum was originally developed by scientists working at the Massachusetts Institute of Technology.

New Tubes

Announcement and data concerning three new transmitting tubes and a new receiving tube have been made available by the RCA Manufacturing Company, Inc., Harrison, New Jersey. These tubes are as follows:

RCA–833–A, a transmitting triode which is similar to RCA–833 but which has an improved construction and can be operated at higher output with forced-air cooling.

RCA–1627, a transmitting triode the same as RCA–810 except that it is designed with a filament rated at 5 volts, 9 amperes.

RCA–8003, a transmitting triode having a maximum plate dissipation of 100 watts. In self-rectifying oscillator circuits such as those used in therapeutic applications, two 8003's are capable of delivering a useful power output (at 75 percent circuit efficiency) of 375 watts.

RCA–12A6, a beam power amplifier of the metal type with a 12.6-volt, 0.15-ampere heater for use in a.c./d.c. receivers. With 250 volts on plate and screen, the 12A6 can handle a power output of 2.5 watts with 10 percent distortion.

Contributed Original Research

A New Method for the Calculation of Cavity Resonators

W. C. Hahn
Engineering General Department, General Electric Company, Schnectady, New York
(Received May 24, 1940)

This article gives a series method for the calculation of the fields in certain circularly symmetric resonators. By the use of some new functions, partial tables of which are included, the necessary series are made to converge rapidly enough so that the method becomes useful for numerical calculations of resonance conditions and wall currents.

IN the development of short wave tubes one of the problems requiring considerable attention is that of the radiofrequency circuits. This is essentially true because the size of these circuits becomes large enough compared to the wave-length so that their calculation is really a field problem rather than a circuit problem. In the intermediate range from a meter down to about ten centimeters wave-length it has been possible to approximate the field effect, reducing everything to a circuit, for certain practical configurations. At 10 centimeters and below these approximations rapidly become invalid, for the desired sizes of resonators. Thus an exact and rigorous method of calculation[1] is almost a necessity, either for use directly in design, or if too cumbersome for this, for justifying new approximations which will allow reasonably simple design formulae. The method to be described seems to meet these requirements, at least for those applications made so far.

The finding of a solution which everywhere satisfies the boundary condition is, of course, the end sought. It would be quite convenient if this solution were in closed form but that does not seem to be the case. Thus the alternative is to put it in the form of an infinite series chosen so as to converge quite rapidly, reducing the labor to a minimum. It is to be emphasized that comparison of the various series solutions which can be obtained is to be made on this basis.

[1] This problem was considered by W. W. Hansen (J. App. Phys. **10**, 38 (1939)) who used certain approximations. L. V. King (Phil. Mag. **21**, 128 (1936)) in a static case brings out the requirement of an infinite set of equations.

The method to be described consists of dividing the cavity into two or more spaces, finding series solutions which fulfill the original boundary conditions in each space separately and then matching the solutions at their common surface. Depending upon how the cavity is divided, different series will be obtained. The matching problem will probably be simplest if the surface is such as to give a sinusoidal variation of E and H with distance, for then the problem is essentially one of matching Fourier series. The examples to be given are of this type. However, the solution appears as equations containing the known geometric constants in a set of infinite series which converge very slowly. Other types of matching may produce more rapid convergence but this does not appear likely at first glance. It is found, however, that these slowly converging series may be handled by subtracting them from standard series, the sums of which are known and then calculating the differences as new series. These latter converge very rapidly so that if the sum of the standard series were tabulated, the process would be reasonably practical from a numerical standpoint.

As a result it appears that for a practical solution, some new functions must be calculated. For the Fourier series type of matching there is required two new functions, one of which is given. The other has not as yet been tabulated over any range. One of the main objects of this paper is to show the usefulness of the method so that these functions may be investigated by mathematicians and tabulated in sufficient detail.

Formation of Series Solutions

Consider the resonator shown in Fig. 1. This resonator has circular symmetry and the outer surfaces are assumed to be perfect conductors. Now divide the space into two parts with the imaginary cylindrical surface G, making the two spaces A and B. Take the origin at 0, positive Z to right along the axis and the resonator to be symmetrical about the plane through 0 perpendicular to the axis.

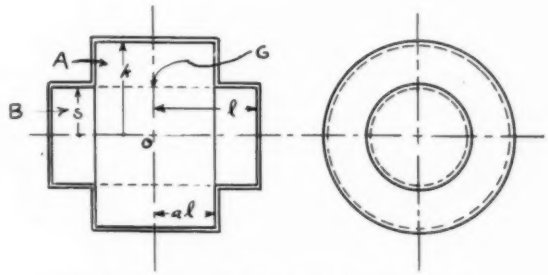

Fig. 1. Resonator with circular symmetry.

Consider space A. A solution of Maxwell's equations which can be used is[2] (in H.L.U. units)

$$E_Z=[F_AJ_0(T_Ar)+G_AN_0(T_Ar)]\cos\gamma_AZe^{i\omega t}, \quad (1)$$

$$E_r=(\gamma_A/T_A)[F_AJ_1(T_Ar)+G_AN_1(T_Ar)]\sin\gamma_AZe^{i\omega t}, \quad (2)$$

$$H_\phi=(i\omega/cT_A)[F_AJ_1(T_Ar)+G_AN_1(T_Ar)]\cos\gamma_AZe^{i\omega t}, \quad (3)$$

the determinantal equation

$$T^2+\gamma^2-\omega^2/c^2=0, \quad (4)$$

and the boundary equations

$$J_0(T_Ak)/N_0(T_Ak)=-G_A/F_A, \quad (5)$$

$$\gamma_A=n\pi/al, \quad (6)$$

where J_p and N_p are the Bessel and Neumann functions of the pth order and n is an integer including zero. Substitution of Eq. (6) in Eq. (2) will be seen to meet the E_r boundary conditions. Substitution of Eq. (6) in Eq. (4) gives

$$T_A=[(\omega/c)^2-(n\pi/al)^2]^{\frac{1}{2}}, \quad (7)$$

which determines T_A. Then all constants of Eqs. (1), (2) and (3) are determined except the amplitude F_A. Thus there is an infinite number of solutions corresponding to different values of n which satisfy the boundary conditions. This infinite series will be taken to represent the solution and what is required now is the amount of each component present.

Now for space B, a similar set of solutions apply. In this case, since the axis is involved $G_B=0$ giving

$$E_Z=F_BJ_0(T_Br)\cos\gamma_BZe^{i\omega t}, \quad (8)$$

$$E_r=(\gamma_B/T_B)F_BJ_1(T_Br)\sin\gamma_BZe^{i\omega t}, \quad (9)$$

$$H_\phi=(i\omega/cT_B)F_BJ_1(T_Br)\cos\gamma_BZe^{i\omega t}. \quad (10)$$

Note that the making of $E_Z=0$ for $-l<Z<-al$ and $al<Z<l$ is part of the matching process to be taken up later. There is in addition, the equation

$$\gamma_B=m\pi/l, \quad (11)$$

which makes $E_r=0$ at the ends, and the combination of this with the determinantal Eq. (6) to give

$$T_B=[(\omega/c)^2-(m\pi/l)^2]^{\frac{1}{2}}. \quad (12)$$

Note that n denotes the components in space A while m gives these for space B. Also it will be found that as n and m increase in value there is a point beyond which T^2 is negative. It then becomes convenient to replace $-T^2$ by τ^2, T by τ, $J_0(Tr)$, $J_1(Tr)$ and $N_0(Tr)$ by $I_0(\tau r)$, $I_1(\tau r)$ and $K_0(\tau r)$ and finally $N_1(Tr)$ by $-K_1(\tau r)$.

Completing the solution then requires that the A and B series of the E's and H_ϕ shall be matched along the boundary G and that E_Z of space B beyond this shall be zero. This is accomplished as follows.

Matching Solutions

Assume the E_Z in space A along the boundary G is

$$E_{ZA}=\left[A_0+\sum_{n=1}^{\infty}A_n\cos\frac{n\pi Z}{al}\right]e^{i\omega t} \quad \text{for } -al<Z<+al$$
$$=0 \quad \text{for } -l<Z<-al \text{ and } +al<Z<+l. \quad (13)$$

Also assume the E_Z in space B at radius s is

$$E_{ZB}=\left[B_0+\sum_{m=1}^{\infty}B_m\cos\frac{m\pi Z}{l}\right]e^{i\omega t} \quad \text{for } -l<Z<+l. \quad (14)$$

[2] Hahn, Gen. Elec. Rev., **42**, 258 (1939).

Since E_{ZB} is a cosine series, the matching of E_{ZB} to E_{ZA} can be accomplished by a Fourier expansion of E_{ZA} with a period $2al$, the terms of which can then be set equal to the corresponding terms of E_{ZB}, giving

$$B_0=\frac{1}{2l}\int_{-al}^{+al}\left[A_0+\sum_{n=1}^{\infty}A_n\cos\frac{n\pi Z}{al}\right]dZ$$
$$=aA_0, \tag{15}$$

$$B_m=\frac{1}{l}\int_{-al}^{+al}\left[A_0+\sum_{n=1}^{\infty}A_n\cos\frac{n\pi Z}{al}\right]\cos\frac{m\pi Z}{l}dZ$$
$$=\frac{2}{\pi}A_0\frac{\sin\pi ma}{m}+\frac{2}{\pi}\sum_{n=1}^{\infty}(-1)^nA_n\frac{m\sin\pi ma}{m^2-n^2/a^2}. \tag{16}$$

Note that the integration being only between $-a$ and $+a$ automatically makes $E_{ZB}=0$ outside of these limits. Then if the individual amplitudes B_m correspond to A_n as given by Eqs. (15) and (16), the E_Z requirements are completely filled. It is also necessary to match E_r and H_ϕ at the boundary G, but matching one of these will simultaneously match the other. In the present case the choice will be to match the H_ϕ's.

Examining Eqs. (1) and (3) it will be observed that at $r=s$, for each component

$$\frac{H_\phi}{E_Z}=\frac{i\omega}{cT_A}\frac{J_1(T_As)+(G_A/F_A)N_1(T_As)}{J_0(T_As)+(G_A/F_A)N_0(T_As)}=R_A. \tag{17}$$

The particular value of R for the nth component will be labeled R_{An}. Similarly for space B, at $r=s$

$$\frac{H_\phi}{E_Z}=\frac{i\omega}{cT_B}\frac{J_1(T_Bs)}{J_0(T_Bs)}=R_B \tag{18}$$

and for the mth component this will be R_{Bm}. Note that R_{An} and R_{Bm} are, from these equations, perfectly determinate constants. Thus the H_ϕ in space B at $r=s$ will be

$$H_{\phi B}=\left[B_0R_{B0}+\sum_{m=1}^{\infty}B_mR_{Bm}\cos\frac{m\pi Z}{l}\right]e^{i\omega t} \tag{19}$$

and in space A at $r=s$

$$H_{\phi A}=\left[A_0R_{A0}+\sum_{n=1}^{\infty}A_nR_{An}\cos\frac{n\pi Z}{al}\right]e^{i\omega t}. \tag{20}$$

Now the boundary imposes no condition on $H_{\phi B}$ outside the limits $-al$ to $+al$. So the matching will consist in obtaining a Fourier expansion of $H_{\phi B}$ with period and between the limits of $-al$ to $+al$. This can then give the corresponding terms of the series of $H_{\phi A}$. Thus

$$A_0R_{A0}=\frac{1}{2al}\int_{-al}^{+al}\left[B_0R_{B0}+\sum_{m=1}^{\infty}B_mR_{Bm}\cos\frac{m\pi Z}{l}\right]dZ$$
$$=B_0R_{B0}+\frac{1}{\pi a}\sum_{m=1}^{\infty}B_mR_{Bm}\frac{\sin\pi ma}{m}, \tag{21}$$

$$A_pR_{Ap}=\frac{1}{al}\int_{-al}^{+al}\left[B_0R_{B0}+\sum_{m=1}^{\infty}B_mR_{Bm}\cos\frac{m\pi Z}{l}\right]\cos\frac{n\pi Z}{al}dZ$$
$$=\frac{2(-1)^p}{\pi a}\sum_{m=1}^{\infty}B_mR_{Bm}\frac{m\sin\pi ma}{m^2-p^2/a^2}, \tag{22}$$

where Eq. (22) is written for the pth term in the infinite series n. Now the values of B_m from Eqs. (15) and (16) can be substituted in Eqs. (21) and (22). There results, after some rearrangement

$$\frac{\pi^2}{2}\frac{R_{A0}}{a}=\frac{\pi^2}{2}R_{B0}+\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2}+\sum_{n=1}^{\infty}\frac{(-1)^nA_n}{n^2A_0}\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2/n^2-1}, \tag{23}$$

$$\frac{\pi^2(-1)^pp^2}{4a}\frac{A_p}{A_0}R_{Ap}=\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2/p^2-1}+\sum_{n=1}^{\infty}\frac{(-1)^nA_n}{n^2A_0}\sum_{m=1}^{\infty}R_{Bm}\frac{a^2m^2\sin^2\pi ma}{(a^2m^2/n^2-1)(a^2m^2/p^2-1)}. \tag{24}$$

Since p is one of the values in the infinite succession n, then Eq. (24) is really an infinite set of equations in which p takes on successively all such values. These equations can then be treated as a set of simultaneous linear equations involving variables A_p/A_0 which may be solved for providing the equations converge to a solution. Inserting the values in Eq. (23) then gives an independent equation which must be satisfied. In this case it is convenient to look upon the satisfaction of Eq. (23) as indicative of resonance.

While formally the solution would be completed by proof that the solution of Eqs. (23) and (24) *does* converge to an answer, such proof is easily obtained in any practical case by trying it. Of considerably more importance is information concerning the easiest way to handle the equations numerically. First of all, the geometry of the resonator appears chiefly in the constants R_{An} and R_{Bm}. As n and m are increased, T^2 becomes negative and it is found that

$$R_{An}\rightarrow i\omega al/cn\pi$$

and

$$R_{Bm}\rightarrow i\omega l/cm\pi.$$

Thus if the sum

$$\sum_{m=1}^{\infty}\frac{\sin^2\pi ma}{m(a^2m^2/p^2-1)}=S_p(a) \tag{25}$$

were known, the sum

$$\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2/p^2-1}=T_p(a) \tag{26}$$

could be quickly found by calculating the differences between the terms of the individual series, which differences would converge very quickly, and then adding this to the known sum $S_p(a)$. At this point some justification of this assumption is necessary. Many calculations using this method have been made and the following data are relevant. If $l<0.3\lambda$ to 0.5λ, with $0<a<\frac{1}{2}$, and with no dielectric, then one or two terms of R_{Bm} will allow the calculation of $T_p(a)$ with slide rule accuracy if the sum $S_p(a)$ is known. If glass or some dielectric occupies part of the space then more terms may be necessary although 3 or 4 is the maximum number required in calculations thus far made. As a result, the computation of $T_p(a)$ does not offer many practical difficulties.

Equation (24) can be rewritten (by a partial fraction expansion)

$$\frac{\pi^2(-1)^pp^2}{4a}\frac{A_p}{A_0}R_{Ap}=\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2/p^2-1}+\sum_{\substack{n=1\\(n\neq p)}}^{\infty}\frac{(-1)^np^2A_n}{(n^2-p^2)A_0}\left[\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2/n^2-1}\right.$$
$$\left.-\sum_{m=1}^{\infty}R_{Bm}\frac{\sin^2\pi ma}{a^2m^2/p^2-1}\right]+\frac{(-1)^pA_p}{A_0}\sum_{m=1}^{\infty}R_{Bm}\frac{a^2m^2\sin^2\pi ma}{p^2(a^2m^2/p^2-1)^2}. \tag{27}$$

Again let

$$\sum_{m=1}^{\infty}\frac{a^2m\sin^2\pi ma}{p^2(a^2m^2/p^2-1)^2}=U_p(a) \tag{28}$$

and

$$\sum_{m=1}^{\infty} R_{Bm} \frac{a^2 m^2 \sin^2 \pi m a}{p^2 (a^2 m^2/p^2 - 1)^2} = V_p(a). \tag{29}$$

A similar situation exists here as to the rapid convergence of the difference between these series in the case cited. The limits given confine the resonance to the lowest order. For higher orders the length or the outer diameter is a greater part of a wave-length and more terms are required. Ordinarily such resonances are least likely to be required so this is no great disadvantage.

Again, in the range cited, it has been found that the third term on the right-hand side of Eq. (23) is from 5 to 15 percent of the other two terms. With a little experience in calculating the geometry used, it is not difficult to estimate this term with sufficient accuracy for many purposes, thus giving a reasonably rapid method for finding resonance. In this case it will be found that variation in k will have negligible effect on $T_p(a)$ and $V_p(a)$ so the most convenient process is to assume the wave-length and from Eq. (23) obtain R_{A_0}, from which k can be found directly. In all cases tested, the convergence of the infinite set of equations for values of A_n/A_0 was quite rapid, using a cut and try process.

In Table I is given values for $S_p(a)$ as calculated by methods given in the Appendix. Similar treatment of $U_p(a)$ is not available, the only data at hand being the set of values listed in Table I and obtained directly from Eq. (28). Better tables of both $S_p(a)$ and $U_p(a)$ are needed to allow calculation for widely varying kinds of geometry.

Other Kinds and Modes of Resonators

It is, of course, possible to put many of the resonators in Fig. 1 end to end, removing the partitions between, without disturbing the solution obtained for each (they will automatically match at the removed boundaries). The resonator of Fig. 1 can also be operated in another mode in which B_0 and the odd terms of B_m are absent. In a line of such resonators this corresponds to 180 degrees phase shift between adjacent resonators. The solution would proceed as before except that in the resulting equations one finds the series

$$\sum_{m=1}^{\infty} \frac{[1-(-1)^m] \sin^2 \pi m a}{m(a^2 m^2/p^2 - 1)} = 2S_p(a) - S_p(2a). \tag{30}$$

This formula is derived in the Appendix where a recurrence relation for the $S_p(a)$ function is given.

A resonator of considerable interest in the application of velocity-modulated tubes is shown in Fig. 2. Although it is possible to take into account the thickness of the inner extensions, it is not usually necessary. Assuming these are made of infinitesimally thin perfect conductors the mode of solution is as follows. Proceed as before using E_{ZA} to represent the E_Z along the surface G and $H_{\phi A}$ the H_ϕ along the same surface. Values of R_{A_n} are, of course, unknown. Then a separate solution is made matching the E_{ZA} and $H_{\phi A}$ to the E_{ZC} and $H_{\phi C}$ of the outer space C, the R_{cq} of which are known. Then the E_{ZA} and $H_{\phi A}$ can be eliminated easily between the two sets of equations, the resulting equations being, if anything, a little simpler than Eqs. (23) and (24).

Other variations of shape can be handled without great trouble providing the matching is done properly. No general rules can be laid down for this as every case presents somewhat different problems.

Table I.

Values of $S_p(a) = \sum_{m=1}^{\infty} \frac{\sin^2 \pi m a}{m(a^2 m^2/p^2 - 1)}$.

$p=$	1	2	3	4	5	6	7	8	9	
$a=0$	1.22	1.56	1.76	1.90	2.01	2.11	2.18	2.25	2.31	$1.21+\frac{1}{2}\log p$
$\frac{1}{8}$	1.21	1.54	1.75	1.89	2.00	2.09	2.17	2.24	2.29	$1.20+\frac{1}{2}\log p$
$\frac{1}{4}$	1.17	1.51	1.71	1.85	1.96	2.05	2.13	2.18	2.26	$1.16+\frac{1}{2}\log p$
$\frac{3}{8}$	1.10	1.44	1.64	1.78	1.89	1.98	2.06	2.13	2.19	$1.09+\frac{1}{2}\log p$
$\frac{\sqrt{3}}{4}$	1.05	1.39	1.60	1.73	1.84	1.93	2.01	2.08	2.14	$1.04+\frac{1}{2}\log p$
$\frac{1}{2}$	1.00	1.33	1.53	1.68	1.79	1.88	1.96	2.02	2.08	$0.98+\frac{1}{2}\log p$
$\frac{\sqrt{5}}{4}$	0.94	1.27	1.46	1.61	1.72	1.81	1.89	1.95	2.01	$0.91+\frac{1}{2}\log p$
$\frac{3}{4}$	0.86	1.19	1.39	1.53	1.64	1.73	1.80	1.87	1.93	$0.83+\frac{1}{2}\log p$
$\frac{7}{8}$	0.68	0.98	1.17	1.31	1.42	1.50	1.58	1.65	1.71	$0.61+\frac{1}{2}\log p$
1	0.41	0.65	0.82	0.94	1.05	1.13	1.21	1.27	1.33	$0.22+\frac{1}{2}\log p$
10	0	0	0	0	0	0	0	0	0	

Values of $S_0(a) = \sum_{m=1}^{\infty} \frac{\sin^2 \pi m a}{a^2 m^3} = \sum_{m=1}^{\infty} \frac{\sin^2 \pi m (1-a)}{a^2 m^3}$.

$a=$	0	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{3}{8}$	$\frac{\sqrt{3}}{4}$	$\frac{1}{2}$
$S_0(a)=$	∞	17.23	11.63	6.73	5.36	4.21

as $a \to 0$, $S_0(a) \to \left(\log \frac{1}{a} - .338\right)\pi^2$

Values of $U_p(\frac{1}{2}) = \sum_{m=1}^{\infty} \frac{a^2 m \sin^2 \pi m a}{p^2 (a^2 m^2/p^2 - 1)^2}$.

$p=$	1	2	3	4
$U_p(\frac{1}{2})=$	2.23	4.69	7.12	9.54

In treating H_0 waves, it will be necessary to match H_Z and E_ϕ. In this case the treatment will follow the same lines substituting H_Z for E_Z and E_ϕ for H_ϕ. Also the same functions $S_p(a)$ and $U_p(a)$ will be needed. Higher order E and H waves require matching of all four tangential components at the surface G. This greatly complicates the equations and solutions of this type have not been carried through. The result will probably be a doubly infinite set of equations for the wave amplitudes. Since, even in this case, the components to be matched have sinusoidal variations along surface G, it seems probable that the same functions will be required.

Matching in Other Planes

The matching which has been carried out thus far is in a direction in which the variation is sinusoidal. This is, perhaps, the simplest case as it involves only Fourier expansions. In the case of resonators composed of perpendicular planes, the matching along any axis is of this same type. In the circular case, matching along a plane perpendicular to the axis involves Lommel integrals.

Consider the case of the effective capacity at the open end of a transmission line (where the outer conductor is extended indefinitely). Here the solution must be semi-infinite on the Z axis. Possibly Fourier integrals might be used but the obvious attack is to match along a plane perpendicular to the Z axis and located at the end of the inner conductor. For this kind of matching the presence of a coaxial dielectric tube extending beyond the inner conductor complicates the situation. In this case it would be necessary to use a method described previously,[3] in connection with velocity modulation tubes, to carry out the matching. Also, such matching would likely give rise to other kinds of functions than $S_p(a)$.

Conclusion

While no claims can be made as to the general applicability or practicability of this method it has been used fairly extensively. In particular it is the only feasible method at present for predicting losses, not only in the copper usually used, but in glass dielectrics sometimes used with these resonators, in order to excite them more or less directly from an electron beam.

The author wishes to acknowledge the assistance of Mr. R. C. Longfellow in the calculation of the functions, as far as they have been taken.

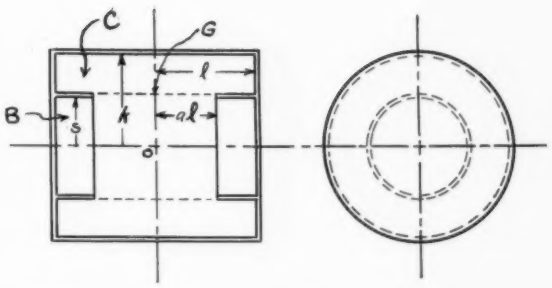

FIG. 2. Resonator of considerable interest in the application of velocity-modulated tubes.

Appendix

Consider the series

$$\sum_{m=1}^{\infty} \frac{\sin^2 \pi ma}{m(a^2m^2/p^2-1)} = S_p(a), \qquad (31)$$

where p is an integer. This series can be shown to be convergent and can be taken as representing a new function $S_p(a)$. The above form is not suited for numerical computation as it converges too slowly in parts of the range.

Now define

$$\sum_{m=1}^{\infty} \frac{(-1)^m \sin^2 \pi ma}{m(m^2a^2/p^2-1)} = S_{-p}(a). \qquad (32)$$

Also define

$$S_p(b, a) = -\frac{(-1)^p p^2 \pi}{a} \int_0^1 \cos p\pi y dy \times \int_0^{(\pi/2)(a+by)} \log \sin x dx. \qquad (33)$$

Then it can be shown that

$$S_p(a) = S_p(-a, a) + S_p(+a, a) \qquad (34)$$

and

$$-\frac{1-a}{a} S_{-p}(a) = S_p(-a, 1-a) + S_p(a, 1-a). \qquad (35)$$

[3] Hahn Gen. Elec. Rev. **42**, 497 (1939).

Also

$$S_p(a)+S_{-p}(a)=S_p(2a), \tag{36}$$

$$S_p(a)-S_{-p}(a)=\sum_{m=1}^{\infty}\frac{[1-(-1)^m]\sin^2\pi ma}{m(a^2m^2/p^2-1)}$$

$$=2S_p(a)-S_p(2a). \tag{37}$$

Now a Maclaurin expansion of the double integral on the right of Eq. (33) could be made. However, the function $\int \log \sin x$ is only analytic for x between 0 and $+\pi$ which limits the utility of the expansion. Consequently $\log \sin x$ is replaced with $\log (\sin x/x)+\log x$. The second term can be integrated by parts, leading to cosine-integral and sine-integral functions. The first term is then analytic from $-\pi$ to $+\pi$ and its integral is expanded in a Maclaurin series. This gives

$$S_p(b,a)=\frac{b}{2a^2\pi}\left\{\begin{array}{l}(-1)^p\log\frac{\pi}{2}(a+b)-\log\frac{\pi a}{2}\\ -(-1)^p\left[Cip\pi\left(1+\frac{a}{b}\right)\right.\end{array}\right.$$

$$\left.-Cip\pi\frac{a}{b}\right]\cos p\pi\left(1+\frac{a}{b}\right)$$

$$-(-1)^p\left[Sip\pi\left(1+\frac{a}{b}\right)-Sip\pi\frac{a}{b}\right]\sin p\pi\left(1+\frac{a}{b}\right)$$

$$+\log\sin a[(-1)^p-1]+\left(\frac{\pi b}{2}\right)^{1}F_a[(-1)^p]$$

$$+\left(\frac{\pi b}{2}\right)^{2}\frac{^2F_a}{\lfloor 2}\left[(-1)^p\left(1-\frac{\lfloor 2}{p^2\pi^2}\right)+\frac{\lfloor 2}{p^2\pi^2}\right]$$

$$+\cdots \tag{38}$$

and thus

$$S_p(a)=-\frac{\log 2\pi p\gamma-Ci2\pi p}{2}+\left(\frac{a\pi}{2}\right)^{1}F_a$$

$$+\left(\frac{a\pi}{2}\right)^{3}\frac{^3F_a}{\lfloor 3}\left[1-\frac{\lfloor 3}{p^2\pi^2}\right]$$

$$+\left(\frac{a\pi}{2}\right)^{5}\frac{^5F_a}{\lfloor 5}\left[1-\frac{20}{p^2\pi^2}+\frac{\lfloor 5}{p^4\pi^4}\right]$$

$$+\cdots, \tag{39}$$

where $\log\gamma=0.577216$ (Euler's constant)

$$S_{-p}(a)=\frac{1}{2}\log\frac{1}{1-2a}$$

$$-\frac{1}{2}\cos\frac{p\pi}{a}\left[Ci\frac{\pi p}{a}-Cip\pi\left(\frac{1}{a}-2\right)\right]$$

$$-\frac{1}{2}\sin\frac{p\pi}{a}\left[Si\frac{\pi p}{a}-Sip\pi\left(\frac{1}{a}-2\right)\right]$$

$$-\left(\frac{a\pi}{2}\right)^{1}F_{(1-a)}-\left(\frac{a\pi}{2}\right)^{3}\frac{^3F_{(1-a)}}{\lfloor 3}\left[1-\frac{\lfloor 3}{p^2\pi^2}\right]$$

$$-\cdots. \tag{40}$$

In the above ${}^qF_d$ represents the qth derivative of $\log(\sin x/x)$ with respect to x and with d substituted for x. In the calculation, the series for $S_p(a)$ converges quite rapidly (4 or 5 terms) for a up to $\frac{1}{2}$ or $\frac{5}{8}$. Above this it becomes more convenient to calculate $S_{-p}(a)$ and then use Eq. (36).

Similarly it can be shown that

$$\sum_{m=1}^{\infty}\frac{\sin^2\pi ma}{a^2m^2}=-\pi^2\log 2$$

$$-\frac{2\pi}{a}\int_0^1 dy\int_0^{\pi ay}\log\sin x dx \tag{41}$$

which, with the same transformation to $\log(\sin x/x)$ and a Maclaurin expansion, gives

$$S_0(a)=\pi^2\left\{-\log 2\pi a+\frac{3}{2}+\frac{(\pi a)^2}{36}\right.$$

$$\left.+\frac{(\pi a)^4}{2700}+\frac{(\pi a)^6}{79380}+\cdots\right\}. \tag{42}$$

Also

$$S_0(a)+S_{-0}(a)=S_0(2a) \tag{43}$$

as before.

Similar attempts on the $U_p(a)$ functions have led to series that converge faster apparently but actually involve small differences so the advantage is more apparent than real. Calculations so far made indicate that the $U_p(a)$ functions do not change very rapidly for $a<\frac{1}{2}$. This has allowed some approximations but there is need for a good tabulation of these functions.

Sputtering and Secondary Electron Emission of Metals Bombarded by Argon Ions

GREGORY TIMOSHENKO*
Department of Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts
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A method has been devised for accurate determination of the absolute rate of sputtering, i.e., the measurement of the number of atoms liberated from a metallic target under the impact of a single ion of known energy. The accuracy of this measurement was 6 to 7 percent—a precision hereto unattainable by other methods. The apparatus producing argon ions consisted of a strong ion-source of capillary-arc type. The ions were accelerated within a high vacuum chamber through a potential, which was varied from 2000 to 7000 volts, and then allowed to strike a metallic target. The sputtering rate was determined by measuring the positive ion current to the target and the loss of target material. Results are given on sputtering of silver by argon, and on the secondary electron emission from aluminum and molybdenum.

INTRODUCTION

THE multitude of articles on sputtering indicates to some extent the complexity of this phenomenon. A general summary on sputtering has been recently presented by Glockler and Lind,[1] while the work on some related processes has been summarized by Willey.[2]

The process of disintegration of metals under the impact of gaseous ions is called "cathode sputtering" as it was first observed on cathodes of gaseous discharge tubes. It is evident, that sputtering is a phenomenon encountered universally in the field of electrical conduction through gases, and in all of its engineering applications. Deactivation of thoriated filaments, transition from glow to arc discharge, back-fires in Hg vapor rectifiers, and other electrical discharge phenomena have been attributed to sputtering.

Today, there exist four major theories of sputtering by Kingdon and Langmuir,[3] Lamar and Compton,[4] v. Hippel,[5,6] and Starr[7] to explain what exactly takes place when a piece of metal is being sputtered. The wealth of available experimental material shows wide disagreement in results obtained by different investigators,[1] and thus it had been difficult to correlate all the data observed, and definitely to prove or disprove in this manner the existing theories of sputtering.

In view of this it seemed desirable to develop a method of accurate measurement of the sputtering rate of metals bombarded by gaseous ions; that is, to determine the amount of material sputtered as a function of the number and of the energy of the bombarding particles. To achieve this, the author chose a simplified experimental arrangement which consisted in bombarding metal targets placed in high vacuum by gaseous ions emerging from a powerful ion-source of capillary arc type.

In the following are described difficulties arising in the determination of the sputtering rate, as well as a number of processes which occur during sputtering. These facts have to be borne in mind during the ensuing discussion of the method of measurement used by the author, together with the obtained experimental results.

FACTORS AFFECTING THE APPARENT SPUTTERING RATE

The majority of experiments on the determination of sputtering rate have hereto been carried out in the glow discharge. In this case there is a great uncertainty as to: (1) the energy of the ions impinging upon the cathode (2) the fraction of the cathode current carried by positive ions, and (3) the rate of "back diffusion" of sputtered particles to the cathode.[8] Thus the determination of the sputtering rate in the glow becomes extremely difficult.

Other experiments were devised to investigate the deposits formed by the sputtered particles upon a collector, rather than measure the loss of mass by the cathode. These data should have led to the determination of the relative rates of

* Now at the University of Connecticut, Storrs, Connecticut.

sputtering of different materials in various gases. The absolute rate of sputtering could then have been computed in cases where the angular distribution of sputtered particles of the metal was known. Here, however, one is troubled by the occlusion of the gas in the deposit, and by partial disintegration (resputtering) of the collected deposit by negative ions.* In addition, there is no positive evidence that all sputtered particles striking the collector surface stick to it. All this makes the results, obtained by measurement of gain in mass by the collector, uncertain.

The process of formation of negative ions at metallic surfaces which are bombarded by positive ions of the same kind, is not known with certainty. Experiments consisting in bombardment of an undegassed nickel surface by Hg^+ ions of 200 ev energy showed evidence of formation of Hg^- ions. Some of these negative ions possessed a high initial energy, correspondent to 109 ev. These 109 ev were found in excess of the energy which could have been acquired in the electric field of the apparatus.[10] It had been suggested that the Hg^- ion forms when the incoming Hg^+ ion robs the metallic target surface of two of its electrons. The ion rebounds then, conserving a large proportion of the energy it had before the impact.[11] This finding was supported by a theoretical calculation showing that the probability of such a process is high, and that this probability increases with the velocity of the incoming positive ion.[12]

FIG. 1. Side view of the sputtering chamber and the capillary-arc ion source. The source block measures 6 cm on the side.

Other, similar experiments, using Hg^+ ions of 4000 ev energy showed, however, no trace of Hg^- ions after the target surface had been sufficiently burned off by the incoming Hg^+ beam. In this case CO^- ions were found. These lighter ions possessed comparatively low initial energies of 14 to 18 ev, indicating their liberation from the target surface by a sputtering mechanism.[13]

When the initially slow negative ions are formed within a sputtering apparatus, they may subsequently attain high speeds in the existing electric fields. The energy so acquired would enable them to disintegrate the sputtered deposits formed upon a collector and other parts within the apparatus.

The surface of a bombarded target may also be the origin of high energy neutral particles, formed by the neutralization and recoil of the incoming positive ions. In case the mass of the impinging positive ion is small compared to the mass of the target atom, the atom lattice of the target will be disturbed but little by the impact. The majority of the neutralized ions will leave the target at approximately the same angle to the surface normal at which they arrived. There will thus be a preferred direction for the neutral gas particles leaving the cathode.

Some of the neutralized gaseous ions may remain deep in the target material. On the other hand, this process is accompanied by the liberation of gases occluded in the cathode.

In case the mass of the impinging ion is comparable in magnitude to the mass of the target atom, the lattice of the target will be greatly

* The partial disintegration of sputtered deposits has been observed by Johnson and Harris, reference 9, and others. It had been attributed to fast secondary electrons originating at the cathode surface under the impact of positive ions. However, such a disintegration process cannot be caused by electrons at voltages used in their experiments, or in the investigation by the author.

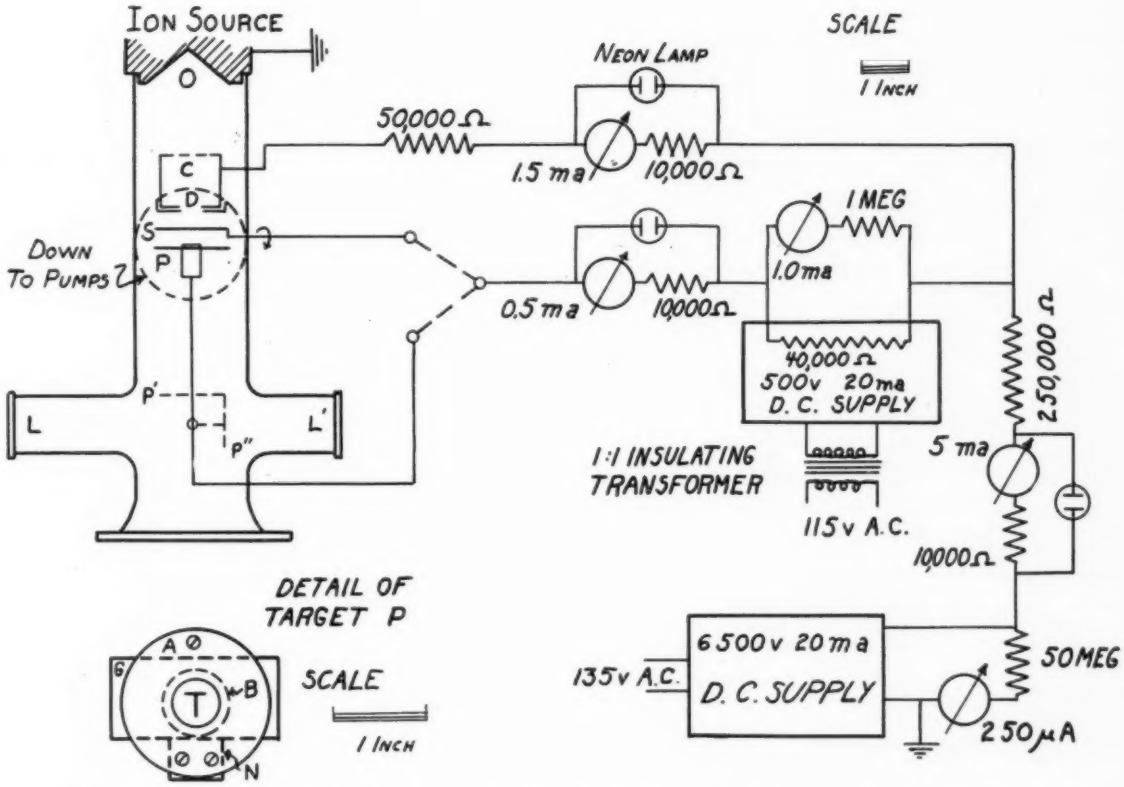

FIG. 2. Horizontal cross section of the sputtering chamber and the electrical measuring circuit. Detail of the bombarded target P is shown at the lower left.

disturbed by the impact and the reflected neutralized ions will stray in a wider angle, and have presumably a characteristic angular distribution.

It had been suggested that these high velocity neutral particles originating at the cathode, and having a characteristic angular distribution, are also responsible for the peculiar forms of disintegration patterns observed upon collectors of sputtered deposits.[8,9] The path of these high velocity neutral particles will not be affected by the existing electric and magnetic fields within the apparatus.

The previously mentioned high speed negative ions coming from the target surface would also possess a characteristic angular distribution similar to that of the reflected neutral particles. In addition to this, they would be influenced by the electric and magnetic fields within the apparatus. The shape and magnitude of these fields are, however, fixed for each particular electrode arrangement, and may be kept the same in a series of experiments. Therefore, the angular distribution of the high speed negative ions will be characteristic of the ratio of masses of the ion and the target atom, and of the target lattice structure. Consequently, the high speed negative ions could also account for the observed disintegration patterns.[9]

The high speed negative ions, if formed in abundance, would also cause an appreciable error in the measurement of the positive ion current flowing to the target. They would not be affected by the small fields used to retard or deflect the secondary electrons originating at the bombarded surface. Application of stronger fields, which would affect the behavior of the high speed negative ions, is however prohibitive, as it would also affect the incoming positive ion beam.

Secondary electrons, originating at the target surface,[14] could also cause an error in the measurement of collected positive ion current. These electrons may, however, be retarded by comparatively small electric fields applied at the target.

The following describes a method of measurement of the sputtering rate of metals under the impact of positive ions. The method allows accurate measurement of: (1) the energy of the impinging ions, (2) the ion current collected by the target, and (3) the loss of cathode material. The effects caused by the neutralized ions, the negative ions, the sputtered particles, and the "back diffusion" of material to the target have been investigated. Tests have also been made of the secondary electron emission from the bombarded targets.

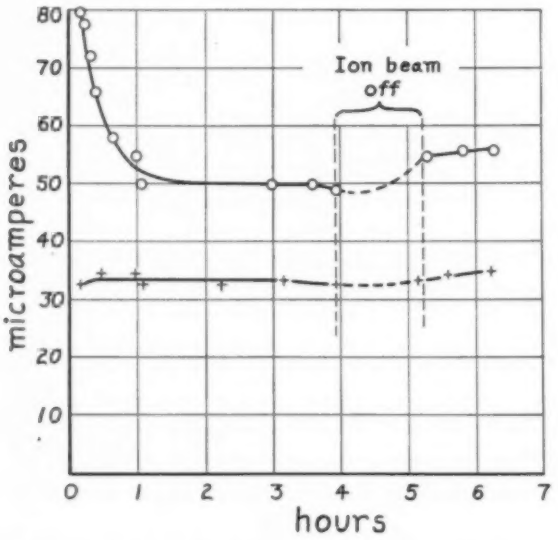

FIG. 3. Conditioning of an aluminum target bombarded by argon ions. ○ denotes the sum of the two currents: the positive ion current flowing into the target and the secondary electron current leaving it, when $V_{cp} = -500$ v. + denotes the collected positive ion current when $V_{cp} = +500$ v. The potential of the focusing cylinder C to ground is -5000 v. Currents are small because of the presence of the diaphragm D.

THE APPARATUS

The sputtering chamber employed, together with the stainless steel ion-source block connected to it, is shown in Fig. 1. A schematized drawing of the horizontal cross section of the sputtering chamber, together with the electrical measuring circuit, is shown in Fig. 2. The ions, entering the high vacuum sputtering chamber at O, were accelerated through the focusing cylinder C and the aperture of the diaphragm D to fall upon electrodes, which were placed at S or P (Fig. 2). The ion-source block was grounded, while the potential V_p of the exposed electrode placed at P could be varied by means of a d.c. power supply from zero to -6500 volts. A smaller d.c. power unit permitted the variation of the potential V_{cp} of S (or P) with respect to C from $+500$ to -500 volts. This change in potential V_{cp} controlled the behavior of the secondary electrons, which were emitted from the exposed electrode under the positive ion impact. The shield-electrode S could be rotated from the outside about a horizontal axis, thus exposing or protecting the electrode P which contained the test target. The design of the target electrode P is shown at the lower left in Fig. 2. It consisted of two aluminum disks A held together by three screws, and fastened to the supporting block N. The disks had circular openings 0.5 inch in diameter, and a glass plate G was clamped between the two disks. The target to be sputtered was then placed between the plate G and the front disk A, exposing an area T to the incoming ion beam. This arrangement permitted an easy mounting of the target and also its quick repeated removal for the purpose of weighing, which was performed outside the vacuum. All other electrodes within the sputtering chamber, as well as their supports were made of aluminum.

The functioning of the capillary-arc type ion source, the gas cleaning procedure, and the pumping arrangement are described in detail in a previous paper by the author.[16]

The gas pressure in the sputtering chamber was maintained during the tests at about 5×10^{-5} mm Hg pressure, and was measured by several types of gauges connected close to the chamber. A very sensitive test for low pressure was provided by the introduction of an iron grid at the bottom of the exhaust sleeve of the sputtering chamber (Fig. 1). The grid was connected through a 0.5-megohm resistor and a microammeter to ground. In case of a poor vacuum a discharge of a few microamperes flowed to the grid. The introduction of this grid also eliminated the spurious currents which could otherwise flow between the high voltage electrodes in the sputtering chamber and far distant parts in the vacuum system which were kept at ground potential.

All microammeters were protected by neon lamps in case of a failure of vacuum. The meters,

together with the 500-volt power supply, were placed on an insulating support. This insured the absence of measurable leakage currents in damp weather even when highest voltages were used.

The focusing of the ion beam was dependent upon the ion-current output of the source, the gas pressure in the sputtering chamber and the potential V_c of the focusing cylinder with respect to ground.[16] The focusing was satisfactory at 5×10^{-5} mm Hg pressure for ion currents up to 250 μA, and for focusing voltages V_c from 2000 to 7000 volts. Under these conditions the current to the focusing cylinder C varied from 0 to 10 μA.

The 50-megohm resistor unit, which was used in the measurement of the high voltage, consisted

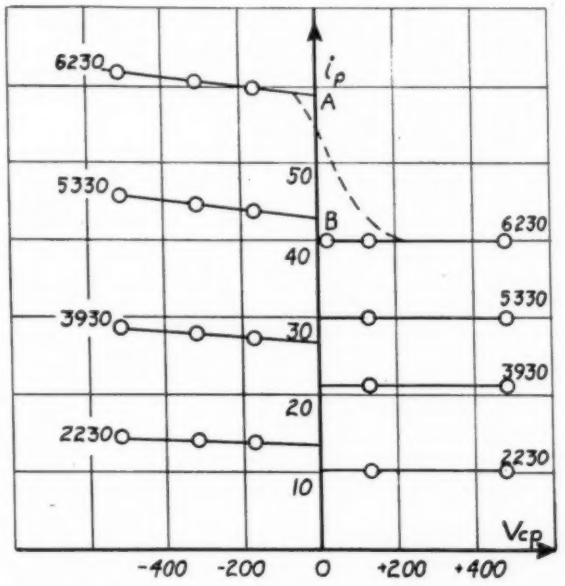

FIG. 4. Volt-ampere characteristics of a conditioned aluminum target bombarded by argon ions of 2230 ev to 6230 ev energy. i_p is the total positive current in microamperes which is flowing into the bombarded target P whose potential V_{cp} with respect to the focusing cylinder C is varied from -400 v to $+400$ v.

of ten resistors, covered by ceresin wax and placed on an insulating support. The power dissipating capacity of this unit was rated at 20 watts. The unit was frequently checked, and calibrated under various atmospheric conditions.

Secondary electron emission

The determination of the current of secondary electrons which are liberated from a target by

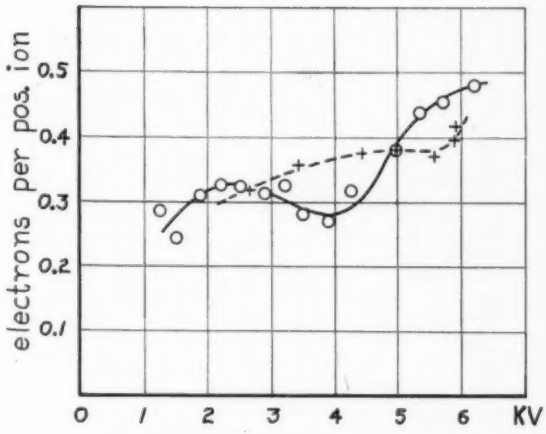

FIG. 5. Secondary electron emission from conditioned aluminum (○) and molybdenum (+) targets as function of the energy of the bombarding argon ions.

the incoming ion beam is difficult if high accuracy of measurement is desired. Numerous investigators found that this electron current varies erratically for the same target surface, and that it is dependent upon the cleanliness of the surface, its temperature, and the time of its exposure to the action of the impinging ion beam.[14,17–21]

The author found that by exposing the target to a strong ion beam of 5000 ev energy, the surface of the target could be conditioned to yield consistent results on electron emission. Figure 3 illustrates the process of surface conditioning, and the "recovery" of the surface when the ion beam has been turned off for some time.

After the target surface has been conditioned, the secondary electron current was determined from curves showing the dependence of the total positive current flowing to the exposed target upon the potential V_{cp} of the target with respect to the focusing cylinder C (Fig. 2). A large number of such curves were obtained for various values of the ion beam accelerating voltages, ranging from 1000 to 6500 volts. Figure 4 shows some of these volt-ampere characteristics obtained with an aluminum target. Similar curves were obtained with a molybdenum target. The electron current leaving the target is equal to AB (Fig. 4), and the number of electrons liberated from the target per impinging positive ion is $AB : BO$. The break in the curves at $V_{cp}=0$ is less pronounced when the diaphragm D is

omitted.* The left-hand as well as the right-hand parts of these curves are very straight. However, a slight displacement in their slopes results in a considerable change in the distance *AB*. Thus the accuracy of determination of the secondary electron current by the above-described method is subject to this inherent error, and this accuracy probably cannot be made better than 5 to 7 percent. Figure 5 shows two curves for the percent of secondary emission from aluminum and molybdenum, computed from the most consistent sets of data. This result indicates that there is apparently no relationship between the shape of the curves and some of the physical properties of the targets, like for example the melting temperature, heat conductivity, etc. Therefore, one has to agree with the finding of Paetow and Walcher[20] who described the secondary electron emission as originating from adsorbed layers on the target surface. Apparently, a layer of gas remains adsorbed on the target surface even if the target has been degassed and its surface burned off by an ion beam.

Results show no change with time in the accommodation coefficient of positive ions on the target surface, as the positive ion current to the target was found to remain very constant (Fig. 3). This is contrary to the finding of Paetow and Walcher, who had observed an increase in the accommodation coefficient of the positive ions.[20]

In case fast negative ions originated at the target surface[10,11] they would not be retarded by the small electric fields applied between the target and the focusing cylinder. This would increase the value of the positive ion current collected by the target. Experiments on sputtering indicate, however, that the fast negative ions could be present only in negligibly small numbers, and that, therefore, the measured positive ion current must be nearly correct.

As to the effect of slow negative ions, which could be liberated at the target surface,[13] they would be retarded by the V_{cp} potential just as are the secondary electrons (Fig. 2). Thus, in the above-described method of measurement, the slow negative ions would be counted as secondary electrons.

The effect of liberation of electrons from the metallic surfaces within the sputtering chamber by photons and metastable argon atoms, which originated in the capillary arc of the source, seemed to be negligibly small. This was indicated by the fact that it was possible to reduce the current to the focusing cylinder apparently to zero, while the cylinder was exposed to a stream of photons and metastables.

As the positive ion output of a capillary arc-type source is very sensitive to impurities which might be present in the gas,[16] the observed constancy of the collected positive ion current served as a good indicator of the reliability of conditions obtained in tests on secondary emission and sputtering.

Sputtering

The study of the secondary electron emission helped decisively in the planning and performance of the experiments on sputtering. Figure 2 shows the final design of the sputtering chamber used in obtaining the further described data on sputtering of silver by argon ions. The target to be sputtered was weighed, then inserted into the target holder (lower left of Fig. 2) and mounted in the sputtering chamber in position *P*. It was protected from impacts of the positive ions by the shield electrode *S*, while preliminary adjustment of the ion beam was performed. The diaphragm *D*, which was used in the determination of secondary electron current, was removed for sputtering tests. Less than one hour's time was needed to obtain steady operation of the ion source. The capillary-arc voltage and current would then remain constant, as well as the arc stabilizing current flowing from the arc anode to the wall of the source block.[16] These conditions insured a steady output of the ion source current which did not fluctuate and needed but little adjustment each half hour. The positive ion current flowing to the shield electrode *S* was measured. Fields up to 500 v were applied between the shield *S* and the focusing cylinder *C* to retard the secondary electrons liberated at the shield surface.

* All registered currents are small in this case because of the presence of the diaphragm *D* (see Fig. 2). The dotted line at the 6230-ev characteristic indicates the shape of the curve when the diaphragm is omitted. In that case, however, the magnitude of the currents becomes much greater.

TABLE I. *Typical data from sputtering tests. These data characterize the steadiness of the test, but the information here contained cannot be used for computations shown below.*

	TIME	V_e*	V_{cp}*	μA TARGET	μA CYLINDER	μA GRID	AMP. SOURCE ARC	MA i_w*	PRESSURES* SOURCE	SPUTT. CHAMBER	SUPPLY
Test No. 4	3:31	3010	+300	220	40	0	1.23	24	75	7.5	5.85
	4:50	3100	+300	220	50	0	1.22	24.5	76	7.5	6.5
	5:37	3150	+300	210	50	0	1.22	25	77	7.5	6.1
Test No. 3	2:10	6000	+500	210	50	0	1.28	25	78	7.5	6.2
	2:50	6050	+500	195	30	0	1.20	28	80	7.0	

Loss in target weight $41.7-36.0=5.70$ mg..... $N_a=3.18\times10^{19}$ (atoms)
Positive charge collected $N_i=\underbrace{199\times10^{-6}}_{\text{current}}\times\underbrace{6}_{\text{time}}\times10^3\times\underbrace{0.557}_{\substack{\text{fraction of current to target proper.}}}=4.25\times10^{18}$ (ions)

$N_a/N_i=7.5$ atoms/ion.

* V_e and V_{cp} uncorrected values. i_w is the arc stabilizing current. Pressures are in arbitrary units.

After steady-state conditions were reached, the target to be sputtered was exposed to the ion beam for several hours. Table I shows typical data recorded in a sputtering test. Time of target exposure was measured easily with high precision between the turning on and off of the high voltage which accelerated the ions onto the target.

The ion beam burned a circular or slightly elliptical spot on the target mount, which was larger than the exposed area to be sputtered. Tests with concentric diaphragms, placed in the path of the ion beam showed that the density of the beam was uniform over its cross section. Thus it was reasonable to assume that the ratio of the burned area B to the exposed circular area T (Fig. 2) would be equal to the ratio of the two currents collected by these areas.* The accuracy of this measurement was augmented by the fact, that in all cases the same area T of the material to be sputtered was exposed, and that all areas of the burns B were nearly of the same size.

After a completed exposure the target was removed from the vacuum chamber and weighed again. The question arose whether the occlusion of the gas in the target during sputtering, and its subsequent exposure to the atmosphere would seriously affect the accuracy of the determination of the mass which was sputtered off. To measure this effect a target was subjected to repeated bombardment by a 6000-ev ion beam, and weighed after each bombardment. The times of target exposure were of various lengths. The result showed that in all cases the ratio of loss in target mass to the total positive charge collected by the target was nearly the same. The values obtained strayed erratically within the limits of the accuracy of the measurement. The measured large loss in sputtered mass, as showed in Table I, makes the effect of gas occlusion upon the weight of the targets negligibly small.

The edges of the glass plate G (Fig. 2) supporting the target showed after numerous sputtering tests that there was only a very small amount of "back diffusion" of sputtered material. Other glass plates placed closely at the target illustrated the same condition.

Tests were made to ascertain whether a resputtering of the material, which left the target and formed deposits elsewhere within the apparatus, took place. Such resputtering would be expected if fast negative ions or fast neutral particles formed at the target surface. The resputtering would cause a partial return of the previously sputtered material to the target surface, and so affect the apparent loss in mass of the target.

A sheet of aluminum, with a few small holes, was substituted for the silver target and was bombarded by ions of various energies for several

* This is in agreement with the computations by Smith and Hartman, reference 23.

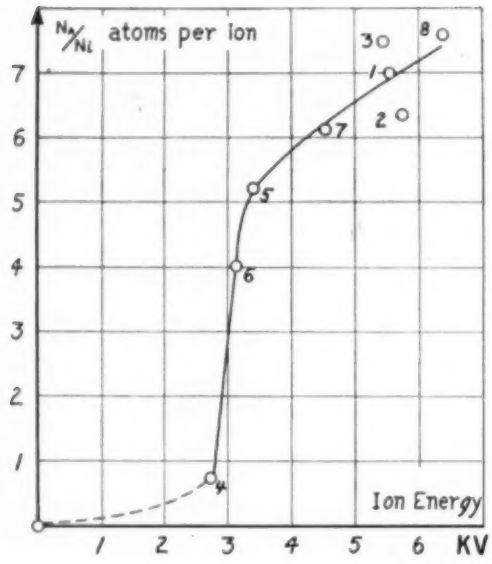

FIG. 6. Sputtering of silver by argon ions. Numbers at the experimental points indicate the sequence of measurements: points 1 to 3—target No. 1, points 4 to 8—target No. 2.

days. The test showed no disintegration of deposits formed at various places within the apparatus, nor did it show any deposits formed on the glass plate which backed up the perforated aluminum target. The absence of resputtering indicates that fast negative ions and fast neutral particles are present in extremely small numbers, if at all, under the conditions of this experiment. The disintegration of deposits as observed by Harris and Johnson[9] could be interpreted as being caused by the originally slow negative ions, which were subsequently allowed to gain high velocities in the electric field of the sputtering apparatus.

The observed slight, "back diffusion" of the sputtered material could be due to a "bouncing around" of the sputtered particles, not all of which adhered to surfaces which they struck in their paths.

The results obtained in sputtering silver by argon are shown in Fig. 6. The accuracy of the determination of the ion charge collected by the sputtered target was within 5 percent, that of the ion energy within 2 percent, and of the loss in mass by the target within 1 percent.

The order of magnitude of the sputtering rate was found to be about the same or somewhat less than that given in various published data. The character of the curve in Fig. 6 indicates that there is perhaps a possibility of interpretation of sputtering on the atomic basis if sufficient data of this type are obtained.

The above-described method is convenient to use for measurement of the sputtering rate of easily sputterable metals, when heavier ions like argon are used for bombardment. One would, however, encounter difficulties in attempting accurate measurements under the conditions of low sputtering rates. For the latter purpose a somewhat different method of measurement may prove adequate. A target to be sputtered is first deposited by evaporation within a high vacuum, and thus its density is easily determinable. Then the target is placed into the sputtering chamber in position p' (Fig. 2) and exposed to the ion beam. After the target had been sputtered to the extent of becoming transparent, it is turned into position p'' and its light transmissivity is compared to that of a standard film of the same material. This comparison may be conveniently done using a precision flicker photometer, which has been developed by the author for this purpose.[24] In this latter type of experiments a good focusing of the ion beam at low voltages and larger distances from the source orifice is necessary.[22,23]

It should be mentioned that the conditions of sputtering in the glow discharge may be quite different, and in that case aggregates of atoms rather than single atoms may sometimes leave the bombarded cathode.

ACKNOWLEDGMENTS

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THERE is no industry today which does not need science to keep pumping red blood into its veins. Where research languishes, industry dies. Research is the life insurance of industrial progress.

DAVID SARNOFF in "Science and Security"

The Measurement of Artificial Radioactivity in Liquid Tracer Samples Using C^{11}

JAMES H. C. SMITH
Division of Plant Biology, Carnegie Institution of Washington, Stanford University, California

AND

DEAN B. COWIE
National Cancer Institute, United States Public Health Service, Bethesda, Maryland

(Received August 16, 1940)

Using C^{11} as tracer for the study of carbon dioxide absorption in plants, unexpected analytical difficulties were encountered. However, a satisfactory technique was developed for the rapid measurement of radioactivity in liquid samples. A degree of precision was obtained so that after the elapse of 6 half-lives (2 hours) the sum of the activities taken from the reaction system was accurate to 1 or 2 percent. This required the determination of an accurate half-life value for C^{11} (20.35 min.). The experimental procedures are described.

INTRODUCTION

THE use of radioactive carbon, C^{11}, promises to yield valuable information concerning the dynamics of chemical and biological processes. Qualitative observations on these processes may be made quite readily, but quantitative results of a precision comparable with that of ordinary chemical analytical procedures may be very difficult to obtain. This was found to be true in our investigation of reactions involved in the absorption of carbon dioxide by sunflower leaves in which an over-all accuracy of the order of one or two percent was desired, and in which the measurement of the radioactivities of solutions was advantageous. The advantage of using solutions lay in the increased speed at which measurements could be made, and speed of measurement is a necessity when an element with a short half-life, such as C^{11}, is being used. To a large extent the difficulties encountered have been eliminated and a method has been developed for determining radioactivity in liquid samples which is both rapid and accurate. This method has been applied to the determination of radioactive carbon dioxide and may be extended to the measurement of the radioactivity of other gases capable of being completely absorbed in solution.

A more precise value of the half-life of C^{11} has also been determined.

REQUIREMENTS FOR TRACER METHODS

The successful use of a given radioactive tracer for reasonably quantitative studies in a chemical or biological process is dependent on a number of factors among which are: possession of a sufficiently long half-life by the element being used; the amount of activity obtainable in the compound to be investigated; the dilution encountered in the reaction being studied; and the freedom from possible disturbance produced by the radioactivity introduced into the chemical or biological system. While these requirements appear to be obvious, efforts made to obtain significant answers to specific problems using the tracer technique have greatly emphasized the necessity for considering these points.

Further technical requirements for actually carrying out the investigation are: (a) an adequately precise value of the half-life of the specific tracer element being used; (b) the elimination of, or correction for, any other radioactivity in the system, e.g., contamination; and (c) a technique of measurement which will give reliable results even after chemical or other types of manipulation.

The precision required (item (a)) for the half-life value of a given tracer depends chiefly upon the ratio of the half-life to the duration of the experiments to be carried out. For example our experiments involving the use of C^{11} in the study of photosynthesis extended over periods of about two hours, i.e., about six times the half-life of the tracer. A small error in an exponent of six has a large effect upon the final result.

The errors in measurement caused by the presence of foreign activities (item (b)) may be very large both in determining the half-life and in

following the tracer element through its various reactions. When measurements extend over periods many times the half-life of the element being traced, obviously the presence of a very small amount of long-lived activity becomes very disturbing. For this reason the tracer element, whenever possible, should be separated chemically from all other radioactive elements before any measurements are made. In cases where this is impossible because of the presence of genetically related radioactive impurities, an accurate analysis of the radioactive decay curve must be made so that the activity due to the tracer element may be determined at any time. Even with accurate knowledge of the complex decay curve of such an element it may be impossible to use such an element in biological experiments because of the error which may be introduced by selective action in the organism on the various radioactive decay products.

It is with the technique of accurate measurement (item (c)) that this paper is primarily concerned. A quantitative method will be described for handling a radioactive gas, $C^{11}O_2$, and measuring its activity in solution.

Choice of Instrument

It should be remembered that no matter what instrument is used for measurement of radioactivity there is inevitably present a statistical variation in the number of particles (N) emitted by the radioactive source of the order of $\sqrt{N}$. Hence about 10,000 beta-particles (from C^{11} for example) must enter the instrument if a precision of 1 percent is desired. A Geiger-Müller counter surrounded by a sample has an ultimate sensitivity on very weak samples of three to possibly five times the ultimate sensitivity of an ionization chamber-electrometer set-up of the type used in this investigation (i.e., a 250-cc ionization chamber containing nitrogen at 25 lb. gage pressure[1] and having a window of 0.1-mm aluminum foil, 8 cm in diameter, connected to a single-fiber Lutz-Edelmann electrometer). For qualitative and semiquantitative analysis this sensitivity of the counter is a great advantage. However, for quantitative work of a precision of 1 to 2 percent the counter has no advantage over the electrometer. This is due to the statistical fluctuation cited, where at least 10,000 counts are needed for an accuracy of 1 percent. This number is as accurately measured on an electrometer as on a Geiger-Müller counter. In our experience, the range of activities over which linearity of response is obtained is several times greater for the electrometer than for the counter. This is of considerable importance when a rapidly decaying sample is being measured and it was because of this advantage that the electrometer was finally selected in preference to the counter for quantitative measurement of the activity of radioactive carbon.

[1] E. Amaldi and E. Fermi, Phys. Rev. **50**, 899–928 (1936). E. Segrè, Nuovo Cimento, **12**, 237–239 (1935).

Experimental Procedure

The labeled sample of carbon dioxide, free from other possible radioactive contaminants, was prepared in the following manner. Anhydrous boron oxide (B_2O_3) was melted onto a thin nickel disk and bombarded with 5 to 10 microamperes of 2-Mev deuterons during a period of from 20 to 40 minutes. The boron oxide glass, containing the radioactive oxides of carbon, was transferred to a combustion furnace and the gases expelled by heating. The oxides of carbon were converted completely into carbon dioxide by passing them over heated copper oxide. The radioactive carbon dioxide was carried into a bulb (approximately 125-cc capacity) by means of air and a measured volume of tank carbon dioxide. After dissolving the carbon dioxide in 5 cc of $N/1$ potassium hydroxide contained in the bulb, the air was expelled from the bulb and all foreign gases removed from the solution by creating a Torricellian vacuum over the solution. After removal of the foreign gases, the carbon dioxide was liberated from the alkaline solution by addition of 5 cc of $2N$ lactic acid. The carbon dioxide liberated was transferred to a graduated gas buret. Usually it was found to contain about 50×10^6 radioactive atoms. This represented a recovery of about 60 percent of the activity of the target. The obtaining of the gas sample from the target required approximately 20 minutes.

All chemical contamination, which might conceivably carry over a trace of spurious impurity, was eliminated by this procedure. This purification proved to be highly significant in defining

the purity of the radioactive gas since in the early experiments of this investigation it was found that the radioactivity of various samples possessed widely diverging half-lives. This indicated the presence, possibly, of different radioactive periods. This possibility was later proved not to be the case and the variations were traced to other causes which will be discussed subsequently.

For measurement of the radioactivity of the samples, an ionization chamber-electrometer setup, previously described, was used. This unit was operated at a sensitivity of *ca.* 2000 beta-particles per division (total beta-ray emission into 4π solid angle). The sensitivity was determined by means of a known uranium standard (1320 beta-particles per second, total radiation). This standard was prepared by distributing the uranium nitrate as evenly as possible in melted paraffin and allowing the paraffin to solidify in a hard-rubber cup, similar to the ones used for measuring the radioactivities of liquid samples. The paraffin was covered with aluminum foil which was sealed in position. This standard was calibrated in terms of a uranium solution of known concentration. Testing by a dilution technique, the response of the instrument was shown to be linear over a 250-fold range of beta-ray intensities. The residual ionization of the instrument was equivalent to a sample with an activity of about 18 beta-particles per second (into 4π) placed in the specified measuring position.

The labeled carbon dioxide was introduced into and recovered from the reaction chamber in gaseous form. It was the activities of these samples which had to be measured. Obviously a choice of methods of measurement was available. The activity of the gas samples could be measured directly, or the gas could be dissolved in alkaline solution and measured in one of the following ways: (a) the activity of the solution could be measured directly; (b) the solution, or a part of it, could be evaporated and the activity of the residue determined; or (c) the carbonate ion could be precipitated and the precipitate dried and its activity obtained.

TABLE I. *Values of half-life of radioactive carbon,* C^{11}.

NUMBER	HALF-LIFE MINUTES	PERIOD OF OBSERVATION MINUTES
1	20.43	125.3
2	20.09	99.5
3	20.93	58.5
4	20.58	103.0
5	20.64	34.0
6	20.33	95.5
7	19.83	54.5
8	20.03	51.0
9	20.30	23.0
Mean value 20.35±0.08 minutes		

Since the direct measurement of the activity of the gas appeared to be less feasible than the measurement of the activities of solutions, only the latter was investigated. Of the three methods mentioned, the last two possessed serious disadvantages. The evaporation of solutions, or precipitation and filtration of solids required time which could be ill afforded. Furthermore, by such procedures equal distribution of material and reproducible placement of the radioactive sample under the ionization chamber so as to yield results of the desired accuracy were difficult to attain. Because it was possible to obviate these difficulties by measuring the activities of solutions directly, a technique was developed for such measurements.[2]

The method consisted in dissolving the sample of labeled carbon dioxide in an alkaline solution and measuring the activity of the solution. The labeled sample of carbon dioxide was withdrawn from the gas buret into an evacuated flask (250-cc capacity) containing 5.00 cc of $N/1$ potassium hydroxide. After complete absorption of the carbon dioxide in the alkaline solution, 4.00 cc of the solution was pipetted into a hard-rubber cup, 4.5 cm in diameter and 0.5 cm deep. The cup was covered with aluminum foil (0.003 in. thick) and placed in the specified position under the ionization chamber. The activity of the solution was then determined.

Some unforeseen difficulties were encountered in measuring the activities of solutions. In the first experiments the hard-rubber cup was covered with Cellophane, but evaporation was too rapid through this cover to permit accurate measurements of activity to be made. This was corrected by substitution of a cover of aluminum foil. The creeping of the solution over the edge of the cup

[2] A method for measurement of radioactivities of solutions by means of the Geiger-Müller counter has been described by W. F. Bale, F. L. Haven, and M. L. LeFevre, Rev. Sci. Inst. **10**, 193 (1939).

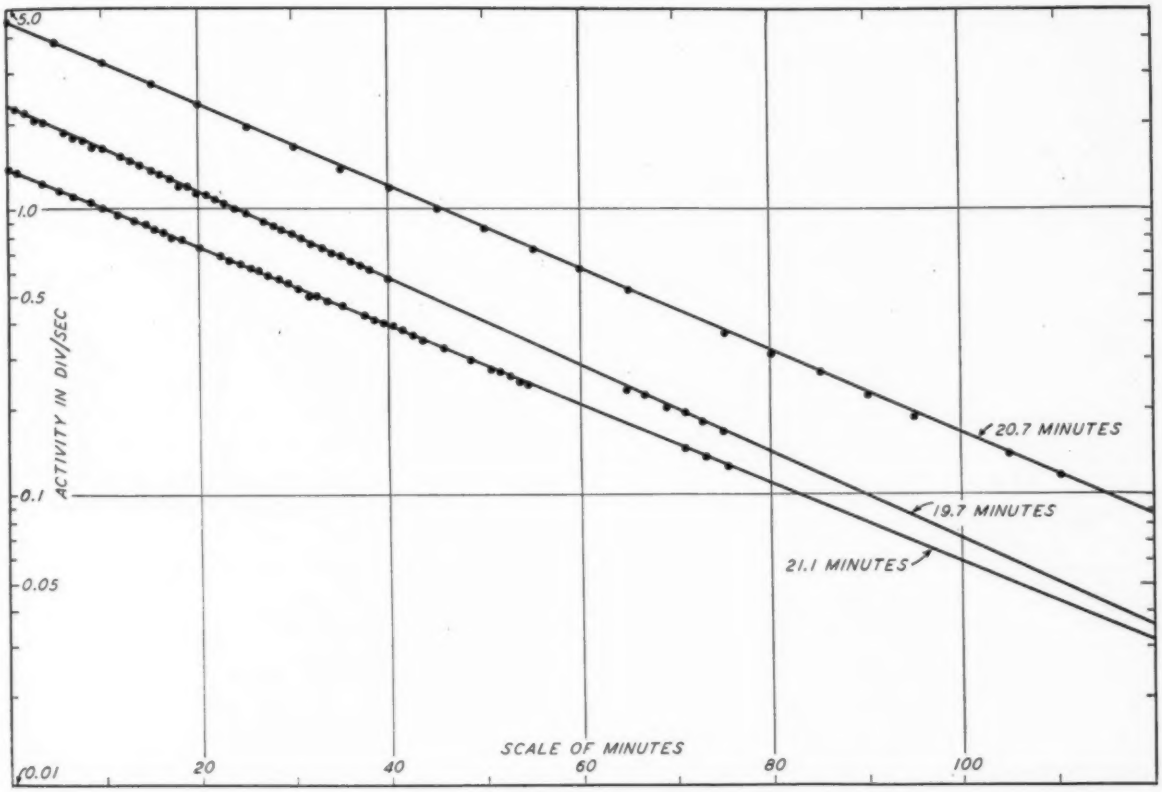

FIG. 1

also proved troublesome. This difficulty was overcome by paraffining the inside of the cup. Paraffining, however, caused the solution to form an irregular and unstable interface between cup and solution. This effect was largely eliminated by touching the solution with a wire barely moistened with olive oil. Changes in temperature and drafts caused erratic behavior of the measuring instrument. These were excluded by inclosing the whole measuring assembly in a cubicle at constant temperature (± 0.5°C, approximate variation). Correction of these difficulties reduced the error of individual readings to ± 1 percent. Of course the time allowed for the individual readings was long enough so that the statistical deviation of N was less than 1 percent.

Washing the hard-rubber cup with water removed all measurable traces of activity. Each cup was checked before re-use.

HALF-LIFE OF C^{11}

Before accurate results could be obtained it was necessary to know the half-life of C^{11} with a relatively high degree of precision. Three values had been reported previously: 20.5 minutes;[3] 20 minutes;[4] and 21.5 ± 0.5 minutes.[5] These values differ significantly, for with a given initial sample the predicted activity at the end of two hours using the value 20 minutes differs by 25 percent from that using 21.5 minutes. It was obvious that for our requirements of accuracy, a redetermination of the half-life constant was imperative.

After the measuring technique just described had been worked out, several determinations of the half-life were made. These determinations are listed in Table I. The mean value obtained, 20.35 minutes, is probably accurate to ± 0.08 minute. The probable error of the individual determinations is ± 0.23 minute, or 1.13 percent.

An analysis of the data obtained in the first experiment in Table I shows that the probable

[3] Don M. Yost, L. N. Ridenour and K. Shinohara, J. Chem. Phys. **3**, 133–136 (1935).
[4] M. L. Pool, J. M. Cork and R. L. Thornton, Phys. Rev. **52**, 239–240 (1937).
[5] S. Ruben, W. Z. Hassid, and M. D. Kamen, J. Am. Chem. Soc. **61**, 661–663 (1939).